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Chemical Market Input/Output Analysis of Selected Chemical Substances to Assess Sources of Environmental Contamination Task I. Naphthylamines

Syracuse Research Corp, N Y

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This report considers the sources of environmental contamination from naphthylamines. Because β-naphthylamine is a proven human carcinogen and there are other alternatives to its use, it is no longer produced and consumed commercially in the United States. However, α-naphthylamine, which is a suspected carcinogen, is still manufactured for use as a chemical intermediate for dyes and herbicides. Thus, this report concentrates on the commercial production and use of α-naphthylamine. Standards established by the Occupational Safety and Health Administration have controlled the occupational exposure to α-naphthylamine and have also had an impact on reducing contamination of the external environment. The OSHA regulations, along with current industry practices, appear to have eliminated the release of α-naphthylamine to the external environment. However, firm conclusions on the potential release of α-naphthylamine from its uses as a chemical intermediate require effluent monitoring data that is unavailable at this time. Further, it is possible that an α-naphthylamine-derived compound could be released to the environment and then degrade to α-naphthylamine. At least two possible sources of this type of contamination seem possible.

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CHEMICAL MARKET INPUT/OUTPUT ANALYSIS OF SELECTED CHEMICAL SUBSTANCES TO ASSESS SOURCES OF ENVIRONMENTAL CONTAMINATION

TASK I. NAPHTHYLAMINES

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TABLE OF CONTENTS

		Page
I.	Introduction	1
II.	History and Future of α-Naphthylamine	2
III.	Market Input/Output	6
	A. Production	6
	B. Importation	6
	C. Use Patterns	10
	D. Exportation	10
IV.	Production Technology	13
	A. Processing Facility	13
	B. Process Description	13
	C. Environmental Management	17
	D. Economics	18
	E. Historical Manufacturers of α-Naphthylamine	19
	1. E.I. duPont de Nemours & Co., Inc.	20
	2. Allied Chemical Co.	21
	3. GAF Corp.	24
V.	Use Process Technology	25
	A. Herbicides	25
	1. Processing Sites	25
	2. Process Description	25
	3. Environmental Management	31
	4. Future Manufacturers	32
	5. Herbicide Uses	32
	a. Historical - Naptalam Use	32
	b. Crop Protection	32
	c. Areas of Usage	34
	6. Economics	34
	7. Alternative Final Use Products - Herbicides	38
	a. Products and Usage	38
	b. Comparative Cost and Persistence	38

TABLE OF CONTENTS
(continued)

		Page
B.	Dyes	44
	1. Processing Sites	44
	2. Process Description	44
	3. Environmental Management	49
	4. Use	49
	5. Economics	56
	6. Alternative Final Use Products - Dyes	64
	7. Alternative Chemicals for Synthesis	65
C.	Discontinued Uses	66
	1. Substituted α-Naphthylamine Derivatives	66
	a. N-Phenyl-α-Naphthylamine	67
	b. N-Ethyl-α-Naphthylamine	68
	c. Sodium Naphthionate (Naphthionic Acid-Sodium Salt)	69
	d. 1-Naphthol-4-Sulfonic Acid (Nevile and Winther's Acid)	70
	e. α-Naphthionic Acid	72
	2. Aldol-α-Naphthylamine Condensate	72
	3. Rodenticide-α-Naphthylthiourea	73
VI.	Material Balance - Exposure to the Environment	75
A.	α-Naphthylamine Manufacture	75
B.	Herbicides	75
C.	Dyes	76
VII.	Environmental Assessment	80
Appendix A		81
Appendix B		89
REFERENCES		91

LIST OF TABLES

Number		Page
III-1	Current Importation of α-Naphthylamine	8
III-2	Importation History of Naphthylamines and Compounds That May Be Derived from α-Naphthylamine	9
III-3	Current Users of α-Naphthylamine	11
III-4	Former Users of α-Naphthylamine	12
IV-1	Data on Current α-Naphthylamine Processing Site	14
IV-2	Historical Manufacturers of α-Naphthylamine	20
V-1	Processing Sites for α-Naphthylamine Herbicides	26
V-2	Annual Production of Naptalam, 1964-1974	31
V-3	Usage of Naptalam in 1971, Quantities & Acres	33
V-4	Usage of Naptalam by States in 1971	35
V-5	1971 Use of Naptalam and Alternative Herbicides	39
V-6	Chemistry of Alternative Products for Naptalam Applications	40
V-7	Alternative Herbicide Products--Comparative Cost and Persistence	43
V-8	Processing Sites for α-Naphthylamine Dyes	45
V-9	Disposal of Dye Wastes	50
V-10	Annual Consumption of α-Naphthylamine Used in Dye Production	51
V-11	Dyes Made Directly from α-Naphthylamine	52
V-12	α-Naphthylamine Dye Producers and Products, 1964-1971	53
V-13	Dyes Manufactured from α-Naphthylamine	57
V-14	1972 DuPont Production Quantities and Values for α-Naphthylamine-Derived Intermediates	66

LIST OF TABLES
(continued)

Number		Page
V-15	Annual Production Quantities of Sodium Naphthionate and Naphthionic Acid	71
V-16	Annual Production Quantities of 1-Naphthol-4-Sulfonic Acid	71

LIST OF FIGURES

Number		Page
II-1	Estimated Current α-Naphthylamine Use	3
II-2	α-Naphthylamine Use in 1972	4
III-1	Production of α-Naphthylamine	7
IV-1	Manufacturing Process for α-Naphthylamine	15
IV-2	Simplified Version of a Partial Melter (Melt Crystallizer)	22
V-1	Manufacturing Process for α-Naphthylamine-Derived Herbicides	27
V-2	Manufacturing Process for α-Naphthylamine-Derived Herbicides	28
V-3	Farm Production Regions	36
V-4	Dye Process Schematic	46

I. Introduction

Compounds α- and β-naphthylamine have recently been regulated by the Occupational Safety and Health Administration (Anon., 1973; Anon., 1974 c) because of their carcinogenic activity. The standards established by OSHA are directed at protecting workers who might be exposed occupationally to the chemicals. However, little thought has been given to the amount of naphthylamines that might be released to the environment and thus indirectly result in human exposure. This report considers the potential for such release of naphthylamines.

Because β-naphthylamine is a proven human carcinogen and there are other alternatives to its use, it is no longer produced and consumed commercially in the United States. However, α-naphthylamine, which is a suspected carcinogen, is still manufactured for use as a chemical intermediate for dyes and herbicides. Thus this report concentrates on the commercial production and use of α-naphthylamine. Small quantities (less than 0.5%) of β-naphthylamine may be found in the industrial grade α-naphthylamine.

II. History and Future of α-Naphthylamine

The past fifteen years have been marked by a decline in the production and in the number of producers of domestic α-naphthylamine. DuPont is the only current U.S. producer of α-naphthylamine, Allied Chemical Corp. and GAF Corp. having halted production in 1970 and 1960, respectively. In the late 1960's and early 1970's, an estimated 5-6 million pounds of α-naphthylamine were being produced annually, but the current annual production level has fallen to an estimated 3-4 million pounds.

Presently, α-naphthylamine is used as a chemical intermediate in the manufacture of pre-emergent herbicides and organic dyes and pigments (see Figure II-1). In the past, a large percentage of the production was used to manufacture dye intermediates (naphthionic acid, sodium naphthionate, 1-naphthol-4-sulfonic acid, N-ethyl-α-naphthylamine) and antioxidants (N-phenyl-α-naphthylamine, aldol-α-naphthylamine condensate) (see Figure II-2). Currently, domestic production of each of these α-naphthylamine derived chemicals has either been terminated or replaced with a process avoiding the use of α-naphthylamine.

The decline in annual α-naphthylamine production is mainly attributable to OSHA's temporary and final standards for α-naphthylamine handling, which were issued May 3, 1973 (Anon., 1973) and January 29, 1974 (Anon., 1974 c), respectively. To a lesser extent, the withdrawal of Allied Chemical Corp. from the production market in 1970 also contributed to the decline. The OSHA standards resulted in the termination of manufacture of all α-naphthylamine derived intermediates and antioxidants and caused 17 of 21 domestic dye manufacturers to cease production of α-naphthylamine derived dyes. They also had an impact upon DuPont's decision to restrict production and handling of α-naphthylamine to the molten form only.

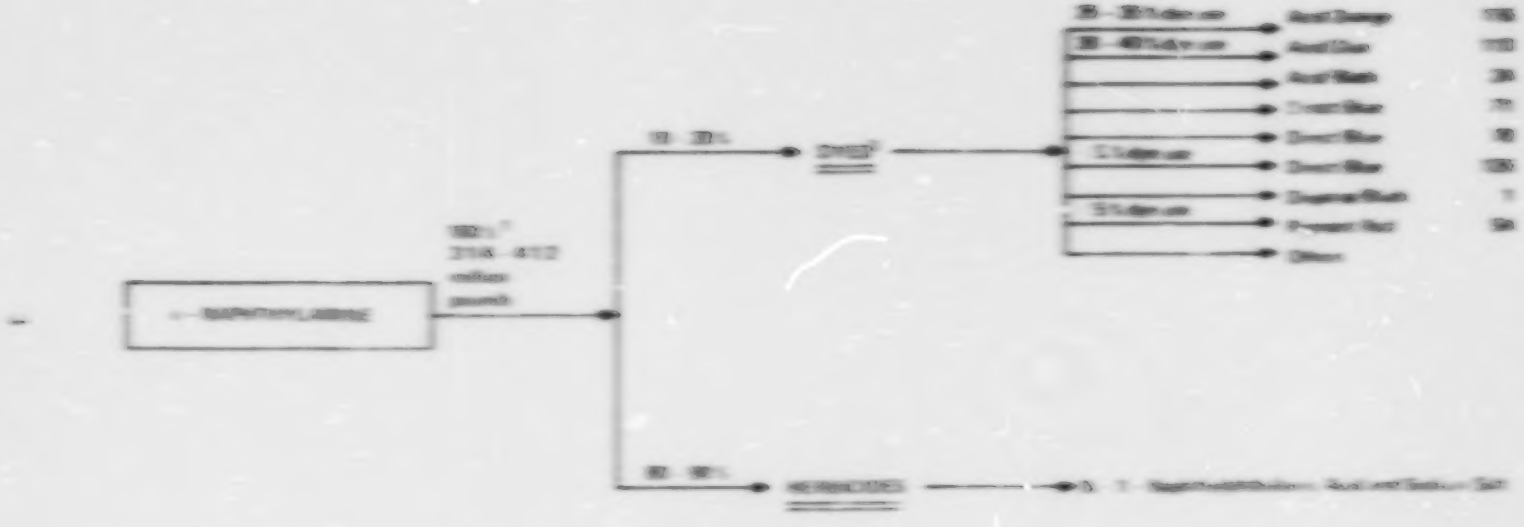


Figure [illegible]. Estimated Current [illegible]

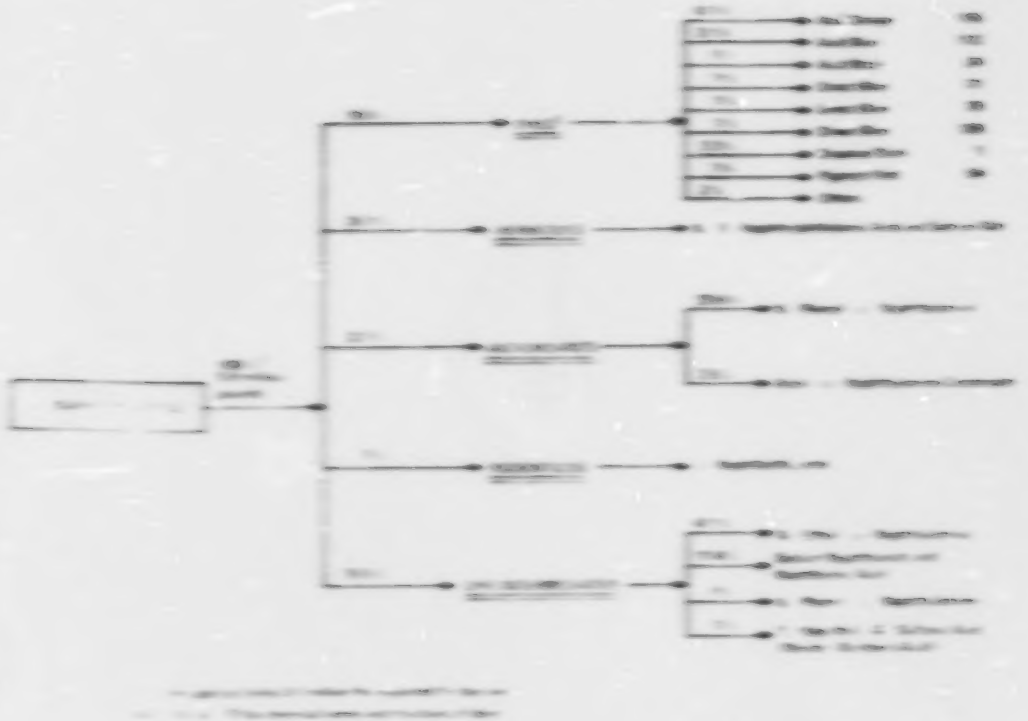


Figure II-1. [illegible]

Historically, α-naphthylamine use in domestic dyes has been stable, with the annual consumption ranging from one-half to one million pounds during 1966-1973. The OSHA standards caused a decline from this range; however, present α-naphthylamine use in dyes is again nearing the one-half million pound mark and current dye manufacturers foresee a slightly expanding market. Three of the four current dye manufacturers import α-naphthylamine in the solid flaked form rather than use the molten form available from Dupont.

Any sizable increase in future domestic production of α-naphthylamine is aligned directly with an increase in production of α-naphthylamine derived herbicides, which use the molten form of α-naphthylamine. These herbicides are used for pre-emergent protection for soybean and peanut crops and are very competitive economically with alternative soybean and peanut herbicides. The soybean and peanut market has expanded greatly in the past five years and, as a result, production of α-naphthylamine derived herbicides has nearly doubled between 1971 and the present. Almost 1.6 million pounds of α-naphthylamine were used in 1971 for herbicides, while approximately 1 million pounds are presently consumed. However, industry spokesmen project only a 25% increase in the next five years.

III. Market Input/Output

A. Production

The E.I. duPont de Nemours and Co., Inc. (processing site located in Deepwater Point, N.J.) is the only domestic manufacturer currently producing α-naphthylamine. DuPont produces a molten form of α-naphthylamine which sells for approximately $1.10 per pound. The current annual production of α-naphthylamine by DuPont is estimated at 3-4 million pounds (SRC estimation).

Former α-naphthylamine producers include Allied Chemical Corp. (Buffalo, N.Y.) and GAF Corp. (Rensselaer, N.Y.). When Allied Chemical was manufacturing α-naphthylamine, it produced about 1 million pounds annually (Allied Chemical Corp., 1975). The GAF production is believed to have been much smaller than 1 million pounds per year.

Figure III-1 illustrates production trends for α-naphthylamine including estimates of future production.

B. Importation

Current and former importers of α-naphthylamine are listed in Table III-1. The available information on past import quantities of α-naphthylamine and its derived intermediates is listed in Table III-2. It should be noted that the data in Table III-2 are based only on surveys conducted at major ports of entry. Among the overseas sources of α-naphthylamine are Poland and Japan (Amitrano, 1975).

A high percentage of imported α-naphthylamine is sold to the dye producers. However, Orien Chemical Corp. (Mueller, 1975) indicates that sales have been made to an additional user for applications other than dyes, but they could not disclose the application because it was considered proprietary.

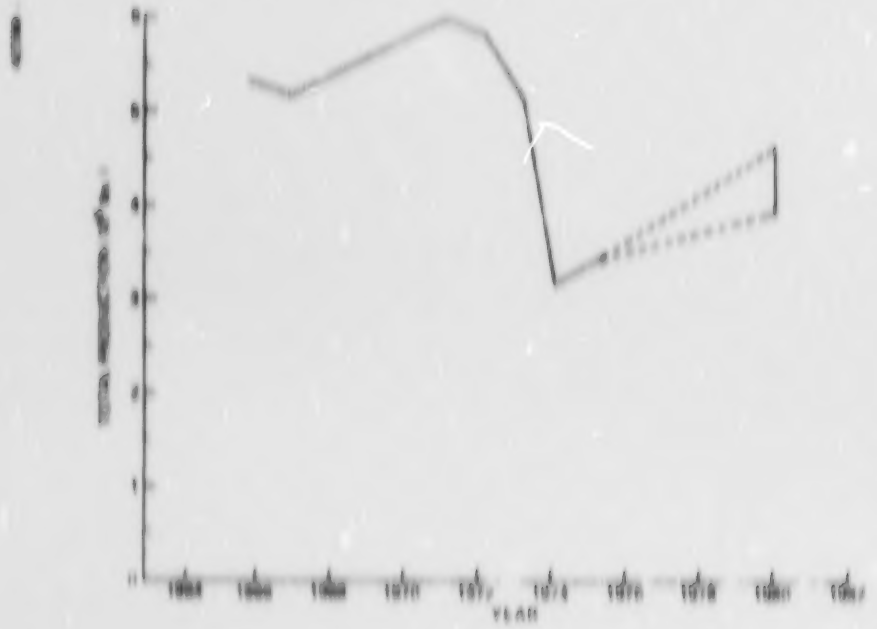


Figure III-1. Production of α-Naphthylamine (SRI Estimations)

Table III-1. Current importation of α-Naphthylamine (OPD Buyer's Guide, 1975-1976; various personal communications)

Current Importers (Amirsano, 1975; Mueller, 1975)	Product Grade	Shipping Containers	Current Annual Quantities
1. Aceto Chemical Co., Inc. (Flushing, N.Y.)	Flaked and Fused	Fiberboard Drums	**
2. Orion Chemical Corp. (Fair Lawn, N.J.)	Flaked	Fiberboard Drums	**
Estimated Total Current Annual Import Quantities:			¼ - ½ million lbs.

Former Importers (Chavkin, 1975; Falieb Chemical Corp., 1975)
1. Riddle-Sawyer Corp. (New York, N.Y.)
2. Falieb Chemical Corp. (New York, N.Y.)

Table III-2. Importation History of Naphthylamines and Compounds That May Be Derived from α-Naphthylamine* (U.S. Tariff Commission, 1967-1973) (All figures in pounds.)

	α-Naphthylamine	β-Naphthylamine	N-Phenyl-α-Naphthylamine
1973	--	--	2,201
1972	89,581	--	--
1971	60,038	--	--
1970	51,980	--	2,205
1969	33,904	--	--
1968	31,257	--	5,070
1967	5,080	38,443	--

	Nevile-Winther's Acid**	Sodium Salt Nevile-Winther's Acid	Sodium Naphthionate
1973	79,466	36,949	501,991
1972	103,449	33,687	1,115,033
1971	26,103	52,381	1,169,253
1970	68,445	--	1,110,614
1969	59,190	--	1,089,492
1968	52,982	--	1,019,879
1967	25,119	--	406,992

* Based only on surveys conducted at major ports.
** 1-Napthol-4-sulfonic acid

C. Use Patterns

Current users of α-naphthylamine are listed in Table III-3, while former users are listed in Table III-4. It can be seen from Table III-4 that 1973 was the year when most terminations occurred. These terminations were precipitated by the issuance of OSHA's regulations (Appendix A) for α-naphthylamine. Most of the users reported that it was not economically feasible to continue use.

D. Exportation

α-Naphthylamine is not and has not been exported in recent history.

Table III-3. Current Users of [illegible]

User	Use	Product Grade	Approximate [illegible] Price (per lb)	Estimated* Current Annual Use (in lbs)
1. Uniroyal Chemical Div. of Uniroyal, Inc.	Herbicides	Molten	$1.10	[illegible]
2. Thompson-Hayward Chemical Co., Subsid., North American Philips Corp.	Herbicides	Molten	$1.15	[illegible]
3. Nelson Chemical Co.	Herbicides	Molten	$1.35	[illegible]
4. GAF Corp.	Dyes	Flaked	$1.45	[illegible]
5. Crompton & Knowles Corp.	Dyes	Molten	$1.10	[illegible]
6. American Color & Chemical Co.	Dyes	Flaked	$1.45	[illegible]
7. Harshaw Chemical Co., Div. of Kewanee Oil Co.	Dyes Pigments	Flaked	$1.45	[illegible]

* SRI Estimation

Table III-4. Former Users of α-Naphthylamine

	User	Product	Year Terminated
1.	Allied Chemical Corp.	Dyes	1971
		Intermediates	1970
2.	American Cyanamid	Intermediates	1971
3.	Atlantic Chemical Corp.	Dyes	1971
4.	Baychem Corp.	Dyes	1971
5.	Benzenoid Organics, Inc.	Dyes	1971
6.	Bernscolor-Poughkeepsie, Inc.	Dyes	1971
7.	Blackman-Uhler Chemical Co.	Dyes	1971
8.	John Campbell & Co.	Dyes	1971
9.	E.I. duPont de Nemours & Co.	Dyes	1971
		Intermediates	1971
10.	Fabricolor, Inc.	Dyes	1971
11.	B.F. Goodrich Co.	Aldol-α-naphthylamine condensate	1971
12.	Hercules, Inc.	Pigment	1971
13.	ICI America, Inc.	Dyes	1971
14.	Mas Mars Color & Chemical Co.	Pigment	1967
15.	Nyanza, Inc.	Dyes	1971
16.	Organic Chemical Corp.	Dyes	1971
17.	G.R. Penick & Co., unit of CPC International, Inc.	α-Naphthylthiourea	1971
18.	Sandoz-Wander, Inc.	Dyes	1971
19.	Sterling Drug, Inc. (Hilton-Davis Chemical Co.)	Pigment	1971
20.	Tennaco, Inc.	Dyes	1971
21.	Toms River Chemical Corp.	Dyes	1971
22.	J.S. Young Co. (Young Aniline Works)	Dyes	1971

IV. Production Technology

A. Processing Facility

Table IV-1 lists data for the DuPont processing site for α-naphthylamine at Deepwater Point, N.J. The information listed includes estimated production quantities, raw materials, production chemistry, and impurity removal and disposal.

B. Process Description

The schematic flow diagram for α-naphthylamine manufacture is illustrated in Figure IV-1.

Naphthalene and mixed acid are added simultaneously to the nitrator at a temperature of 58-61°C. The mixed acid contains nitric acid, 35.5-36.5%, and sulfuric acid, 41.3-42.3%, and the remainder is water. This batch is cooked for thirty minutes at 60-65°C and is then transferred to a gravity separator. In the gravity separator, the mixture separates into two layers, an acid layer and a nitronaphthalene layer. The acid layer, which contains 55% sulfuric acid, is separated off and run to a recovery system. The molten nitronaphthalene is washed with water several times at 55-57°C and is then neutralized with sodium bicarbonate and given a final water wash (Boyd, 1976).

The reaction product, α-nitronaphthalene, is a light yellow, odorless solid which melts at 52°C; the yield is 97.8% of theory (Boyd, 1976). The product will contain 3-5% β-nitronaphthalene and 0.3-1% dinitronaphthalenes as impurities (Donaldson, 1958; Treibl, 1967).

Separation of the α-nitronaphthalene from the by-products is accomplished by a process called "melt crystallization" (Boyd, 1975;1976). This

Table IV-1. Data on Current α-Naphthylamine Processing Site

Company - E.I. duPont de Nemours & Co., Inc.

Site - Deepwater Point, N.J.

Estimated Annual Production - 3-4 million lbs (SRC estimation)

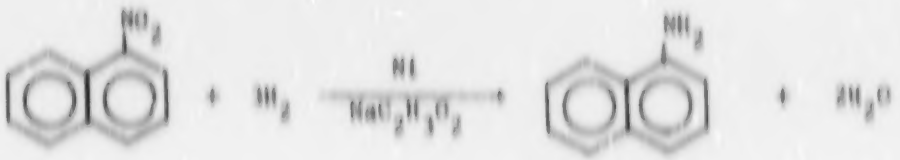
Raw Materials - Naphthalene, Nitric and Sulfuric Acid, Hydrogen Gas, Catalysts (Nickel and Sodium Acetate)

Production Chemistry:

Step #1: Nitration of Naphthalene

1-Nitronaphthalene

Step #2: Reduction of α-Nitronaphthalene



Step #1:	Impurities	Removal Method	Disposal Method
	H_2O and H_2SO_4	Density Separation	To Acid Recovery
	α-Nitronaphthalene	Melt Crystalization	Incineration
	Dinitronaphthalenes	Melt Crystalization	Incineration

Step #2:	Impurities	Removal Method	Disposal Method
	Ni Catalyst	Filtration	Reusable or Buried
	Water (major portion)	Density Separation	Incineration
	(minor portion)	Vacuum Distillation	Incineration
	Still Pot Residues		Incineration

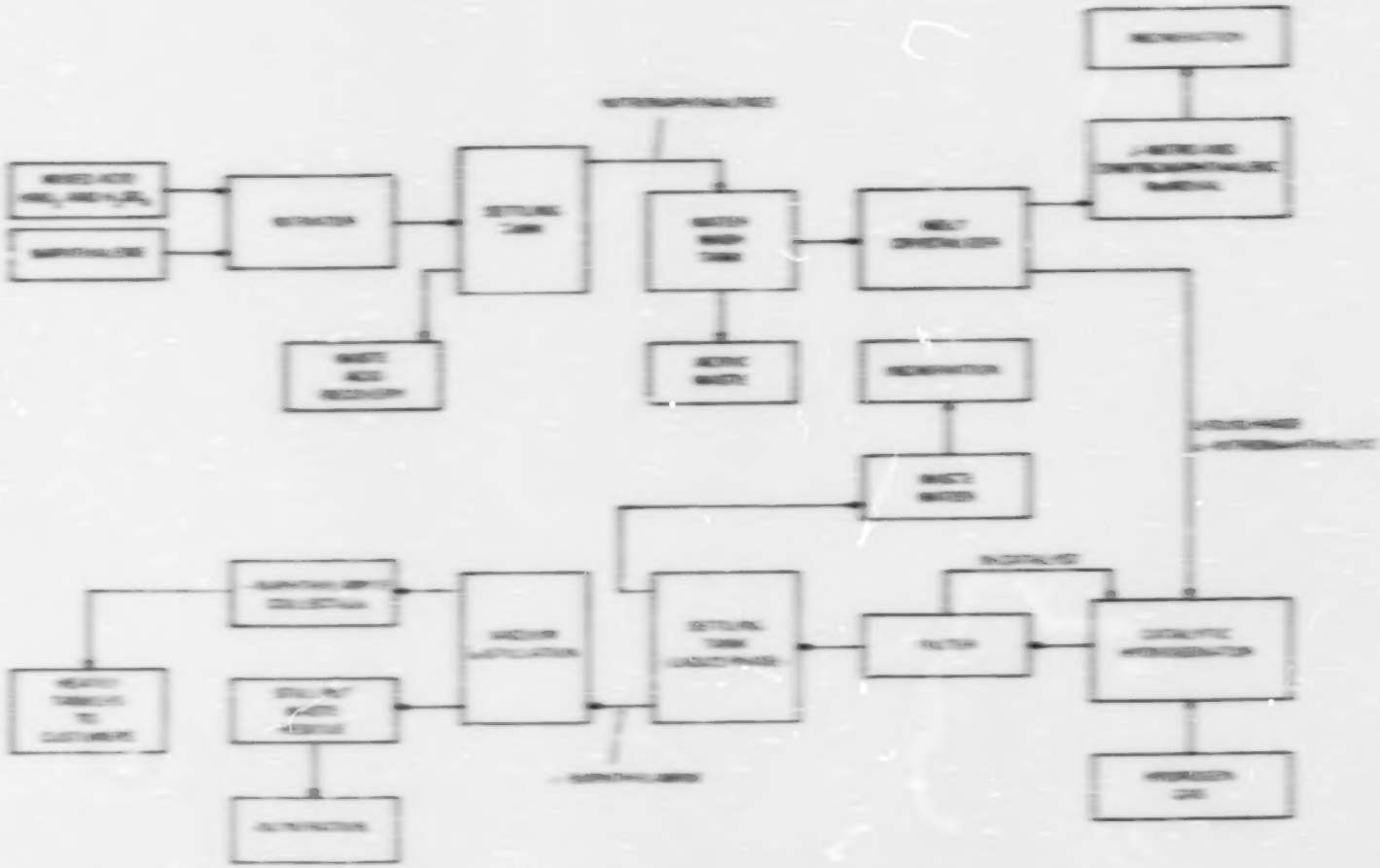


Figure IV-1. Manufacturing Process for o-Nitrotoluene

involves a partial melting or "sweating" of the reaction product.[1] The α-nitronaphthalene and dinitronaphthalenes are collected and incinerated, while the liquid phase α-nitronaphthalene is transferred to a catalytic hydrogenator for reduction (Boyd, 1973-1976).

Reduction of the α-nitronaphthalene to α-naphthylamine is described by the following description of U.S. Patent 2,105,321 which is assigned to DuPont (Henke and Renner, 1938):

> "Alpha nitronaphthalene is reduced to alpha-naphthylamine in the liquid phase with hydrogen. The hydrogenation is preferably carried out at 80 to 100°C and under 400 to 500 pounds hydrogen pressure in the presence of a nickel catalyst. After hydrogen absorption has ceased, the charge is filtered to remove catalyst, and the alpha-naphthylamine is separated from the water layer. The amine thus produced may be further purified by vacuum distillation through a short column. The distilled amine in this liquid state is a colorless product which analyses 99 to 100% naphthylamine."

The patent proceeds to claim (Henke and Renner, 1938):

> ". . . the presence of a nickel catalyst in which the active nickel is about .2% to about .5% by weight of the nitro compound in the presence of water in an amount of about 5% by weight of the nitro compound and in the presence of sodium acetate in the amount of about 0.12% by weight of the nitro compound."

[1] For a detailed description of melt crystallization, see Section IV-E-2.

After the α-naphthylamine has been purified as described by the patent, the molten α-naphthylamine (m.p. 50°C) can be transferred to heated railway or truck tankers for shipment to customers. The shipment requires special labeling and handling instructions (see Appendix B) because the final product may contain up to 0.5% β-naphthylamine, a known human carcinogen. More commonly the product contains 0.4% β-naphthylamine (Boyd, 1975-1976).

The wastes produced from purification of the α-naphthylamine are incinerated to prevent environmental release (Boyd, 1975-1976).

C. Environmental Management

There is no loss or disposal of α-naphthylamine or naphthylamine by-products to the environment from the α-naphthylamine manufacturing process. All of the impurities or waste by-products are collected and incinerated (Boyd, 1975-1976). Some wastes have been buried in landfill approved for carcinogenic materials (Boyd, 1976).

The only other possible route for escape to the environment is from accident or equipment failure.

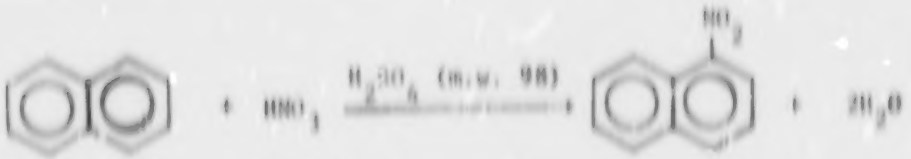
B. Economics

The following is a rough estimate of the material costs for α-naphthylamine production:

Raw Materials & Cost (Chemical Marketing Reporter, 1976)

Naphthalene	$0.136/lb
Nitric Acid	$0.06/lb
Sulfuric Acid	$3.025/lb
Hydrogen	$1.00/lb (Various Personal Communications)

Step #1: Nitration of Naphthalene



(m.w. 128) (m.w. 63) (m.w. 173)

Basis: 1-lb-mole α-nitronaphthalene (100% yield)

Naphthalene	128 lb	= $17.41
Nitric Acid	63 lb	= $ 1.78
Sulfuric Acid	98 lb	= $ 2.45
		$23.64

α-Nitronaphthalene Cost: $23.64/173 lbs or $0.137/lb

Step #2: Hydrogenation of α-Nitronaphthalene

(m.w. 173) (m.w. 2) (m.w. 143)

Basis: 1-lb-mole of α-naphthylamine (100% yield)

α-Nitronaphthalene	171 lb	= $21.64
Hydrogen	6 lb	= $ 6.60
		$29.64

Approximate α-Napthylamine Cost: $29.64/141 lbs or $0.21/lb

This $0.21/lb is material cost only and is an approximation at best. Catalyst costs and sulfuric acid recovery have not been included.

The current selling price of α-naphthylamine is $1.10/lb from DuPont (Boyd, 1975-1976). Mark-up includes costs for labor, equipment, profits, etc. The capital value of the equipment was not available from DuPont. However, all of the equipment used (nitrator, settling tanks, melt crystallizer, hydrogenator, etc.) is used only for α-naphthylamine manufacture. The equipment is not used to produce any other chemicals (Boyd, 1975-1976).

Considering the 1-4 million pound estimation for annual α-naphthylamine production and the selling price of $1.10/lb, the annual value of α-naphthylamine sales would amount to $1.1-$4.4 million.

The selling price of α-naphthylamine in 1972 was approximately $0.55/lb. The price rise is probably attributable to the inflated price for the naphthalene grade required for nitration, the additional safety requirements imposed by the OSHA standards, and diminished sales volume.

E. Historical Manufacturers of α-Naphthylamine

Historical manufacturers of α-naphthylamine, reporting to the United States International Trade Commission from 1960 to 1971 are listed in Table IV-2. Additional data on α-naphthylamine producers are listed below.

1. E.I. duPont de Nemours & Co., Inc. (Deepwater Point, N.J.)

Dupont is the only current manufacturer. In 1972 Dupont produced nearly five and one-half million pounds of α-naphthylamine. Almost half of that production was captively used to synthesize the following intermediates: N-phenyl-α-naphthylamine, N-ethyl-α-naphthylamine, naphthionic acid and sodium salt, β-naphthionic acid, and 1-naphthol-4-sulfonic acid (Nevile and Winther's Acid). DuPont has subsequently terminated captive use of α-naphthylamine. The present estimated (SRC estimation) production of α-naphthylamine has fallen to 1-4 million pounds annually.

Table IV-2. Historical Manufacturers of α-Naphthylamine (United States International Trade Commission, 1960-1973)

1973	DuPont
1972	DuPont
1971	DuPont
1970	Allied Chemical; DuPont
1969	Allied Chemical; DuPont
1968	Allied Chemical; DuPont
1967	Allied Chemical; DuPont
1966	Allied Chemical; DuPont
1965	Allied Chemical; DuPont
1964	Allied Chemical; DuPont
1963	Allied Chemical; DuPont
1962	Allied Chemical; DuPont
1961	Allied Chemical; DuPont
1960	Allied Chemical; DuPont; GAF Corp.

2. Allied Chemical Co.

The Specialty Chemicals Division of Allied Chemical Co., located in Buffalo, N.Y., terminated production of α-naphthylamine in 1970. Production quantities averaged approximately one million pounds per year (Allied Chemical Corp., 1975).

In the Allied process, naphthalene was nitrated via mixed acids (1:1 molar ratio of nitric and sulfuric acids) to nitronaphthalene in a manner similar to that previously described in Section IV-B. Here again, the nitronaphthalene product contained 95-96% α-nitronaphthalene, 3-4% β-nitronaphthalene, and 0.5-1% dinitronaphthalenes. In order to obtain a purified α-nitronaphthalene product, the β-nitronaphthalene and dinitronaphthalenes were separated from the α-nitronaphthalene by a process of partial melting. The flaked nitronaphthalene from the washer was transferred to the partial melter (melt crystallizer)(see Figure IV-2) and allowed to solidify. The melting points of the constituents are as follows: α-nitronaphthalene = 50°C, β-nitronaphthalene = 111°C, dinitronaphthalenes = 144 to 217.5°C. Steam was then injected through pipes which were interspersed in the mass of solidified nitronaphthalene, and the temperature was allowed to rise to several degrees above the melting point of the α-nitronaphthalene (50°C). The α-nitronaphthalene melted, and the less dense β-nitronaphthalene and dinitronaphthalenes solids floated to the top of the mass and were skimmed off and incinerated. The temperature was then dropped below the 50°C mark until solidification began and then raised above that mark once more. A second skimming was done to remove any remaining β-nitronaphthalene and dinitronaphthalenes; however, this second skimming also removed sizable amounts of α-nitronaphthalene, so

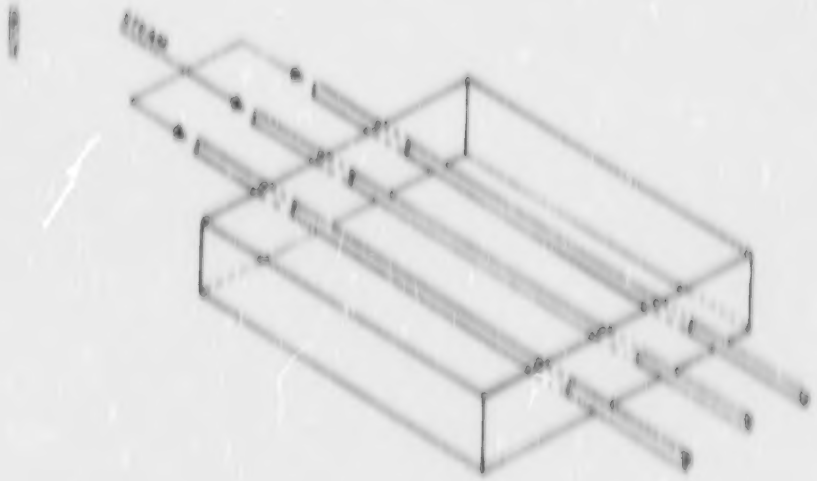
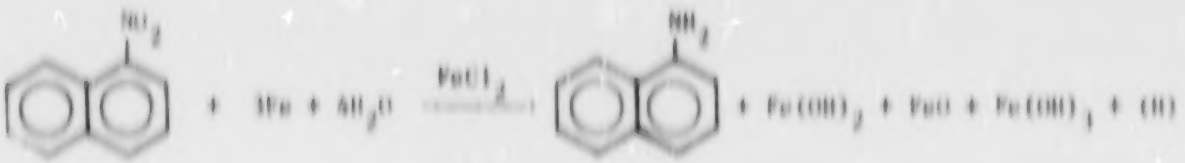


Figure IV-2. Simplified Version of a Partial Melter (Melt Crystallizer)

the second skimming was saved for addition to the next batch of unpurified nitronaphthalene. It is assumed that the DuPont melt crystallization step is very similar to the process used by Allied.

The purified α-naphthylamine was then reduced to α-naphthylamine by the Bechamp iron reduction process. A ferrous chloride solution (made from 1% hydrochloric acid and 20% mesh iron) was charged into water and the mixture was heated to a boil. Equal weights of molten α-nitronaphthalene and fresh iron borings were added to the boiling solution. After several hours of heating under reflux, the reduction was complete and Na_2CO_3 was added to neutralize the $FeCl_2$. The α-naphthylamine and water were distilled under vacuum. The overall reaction proceeds approximately according to the following equation (Shreve, 1961):



$$+ \ 3Fe + 4H_2O \xrightarrow{FeCl_2}$$

$$+ \ Fe(OH)_2 + FeO + Fe(OH)_3 + (H)$$

$$Fe(OH)_2 + Fe(OH)_3 \longrightarrow Fe_3O_4 + 4H_2O$$

The α-naphthylamine was separated from the water solution by a flash distillation process and stored in the molten state (approximately 99.7% pure). Unreacted iron borings were recovered and reused. Overall yield of α-naphthylamine ran about 85-90% based upon initial naphthalene starting material.

Approximately one-half of the Allied Chemical α-naphthylamine was shipped in molten form via tankers to herbicide manufacturers. A large portion of the remaining one-half was sulfonated to produce naphthionic acid and sodium naphthionate for use in dye manufacture, especially for F & DC Red No. 2. A very small portion of the α-naphthylamine was used to make the dye intermediate 1-naphthol-4-sulfonic acid (Neville and Winther's Acid). The remaining α-naphthylamine was flaked for captive dye production and for sale (fiber drums) in the open market.

3. GAF Corp. (Rensselaer, N.Y.)

GAF Corp. terminated production in 1960. It is believed that GAF production was used captively to produce dyes, although no production figures were available. Because consumption was mostly for dyes, the amount of α-naphthylamine made by GAF was probably insignificant as compared to DuPont and Allied.

V. Use Process Technology

A. Herbicides

1. Processing Sites

Present processing plants, which manufacture herbicide products from α-naphthylamine, are listed in Table V-1 by company, product, and estimate of production volume.

2. Process Description

Only one herbicide ingredient derived from α-naphthylamine is domestically produced; it is commonly called naptalam (N-1-naphthylphthalamic acid). The various products listed in Table V-1 are all formulations derived from naptalam. The general process flow diagrams for naptalam production are illustrated in Figures V-1 and V-2. The only major difference in the process diagrams is the method for separating the naptalam from the reaction medium.

The α-naphthylamine, which is shipped to the herbicide producers in a molten state via railroad or truck tanker, is pumped directly from the tanker into a stainless steel reactor. The reactor has been previously charged with a solution of phthalic anhydride in benzene, xylene, or kerosene. The benzene, xylene, or kerosene solvents are used because both phthalic anhydride and α-naphthylamine are soluble in them. The α-naphthylamine and phthalic anhydride react to produce N-1-naphthyl phthalamic acid (naptalam) according to the following equation:

N-1-naphthylphthalamic Acid
(Naptalam)

Table V-L. Processing Sites for α-Naphthylamine Herbicides

Company	Site	Products	Estimated* Production, Active Ingredients, lbs
1. Universal, Inc. Universal Chemical, division	Gastonia, NC	Alanap Dynap Naptalam-Sodium Solo	4 Million
2. North American Philips Corp. Thompson-Hayward Chemical Co., subs.	Kansas City, KS	MPA-3	1 Million
3. Helena Chemical Company	W. Helena, AR	Amtrak Marauder	1 Million

* SRI estimates

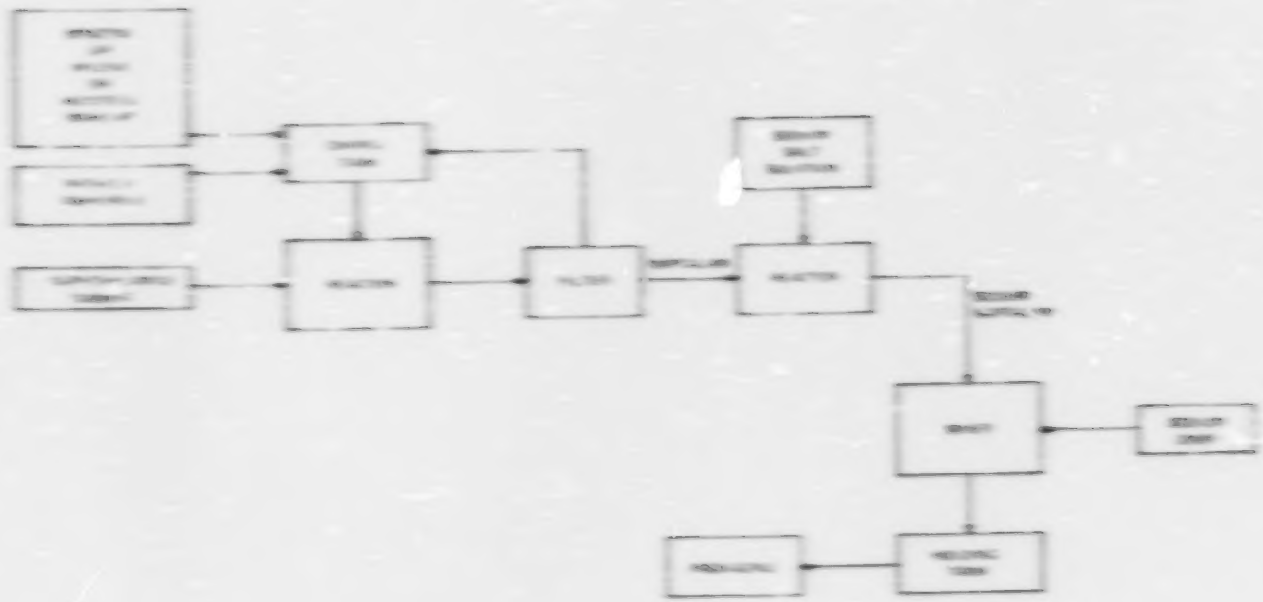


Figure 1-1. Manufacturing Process for α-Naphthylamine-Derived Herbicides (adapted from information from Smith and Hoffman, 1978; various personal communications; SRC Estimations)

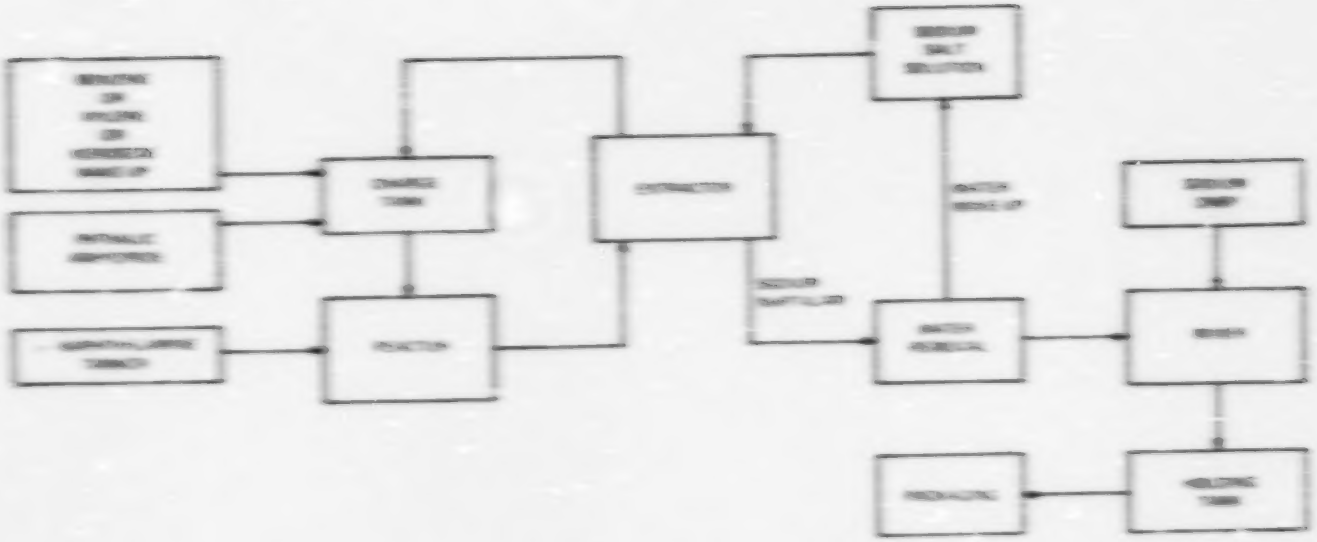
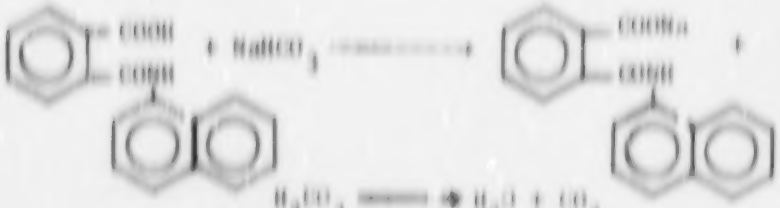


Figure 1-1. Manufacturing Process for ε-Caprolactam-Derived Nonfibers (adapted from information from Smith and Hoffman, 1956; various personal communications; SRC Incinerations)

The naptalam, which is nearly insoluble in the organic solvent, precipitates out of the solution. The reaction is carried out at room temperature and atmospheric pressure (Smith and Hoffman, 1950).

The naptalam can now be separated from the organic solvent by filtration or extraction as illustrated in Figures V-1 and V-2, respectively. In the filtration process, the naptalam is collected from the filters while the organic solvent is recycled to the reactor and reused. The water insoluble naptalam is now converted to water soluble naptalam (sodium N-1-naphthylphthalamate) by reaction with solutions of either sodium hydroxide or sodium bicarbonate.

(1)

(2) 

$$H_2CO_3 \longrightarrow H_2O + CO_2$$

Although any sodium base can theoretically be used, selection is probably based upon cost.

In the extraction process, separation from the organic mixture and conversion to sodium naptalam can be accomplished in a single step. The organic solvent, containing the precipitated naptalam, is contacted with the alkaline aqueous solution and the naptalam forms the sodium naptalam which dissolves into the water phase. The organic solvent is recycled to the reactor for reuse while the sodium naptalam solution, the desired product, is collected

for formulation into the final herbicide product. The sodium naptalam solution may be concentrated by water removal via contact evaporators or other common water removal equipment.

It should be noted that naptalam is unstable in aqueous solutions with a pH greater than 9.5 and temperatures above 200°C. At a pH more alkaline than 9.5, naptalam will hydrolyze to α-naphthylamine (Smith and Stone, 1950; Spencer, 1968).

The sodium naptalam solution is used to formulate the herbicide products. A straight sodium naptalam solution, two pounds sodium naptalam per gallon, is marketed under the tradename Alanap® by Uniroyal. However, more than 90% of the sodium naptalam produced is formulated with the sodium salt of DNBP (sodium 4,6-dinitro-2-sec-butylphenate) (Dowling, 1975). DNBP (4,6-dinitro-2-sec-butylphenol) is a herbicide marketed by Dow Chemical with the common name dinoseb. The resulting formulation is a mixture of two pounds sodium naptalam plus one pound sodium DNBP per gallon (Anon., 1974 a). This particular mixture is marketed under the following tradenames and companies: Dyanap® (Uniroyal), Ancrak® (Ansul Co.), NPA-3 (Thompson-Hayward), and Marauder (Helena Chemical Co.).

It should be noted that the Ansul Co. does not manufacture their product (Nicklaus, 1975). The Ancrak® is manufactured by the Helena Chemical Co. for the Ansul Co. (Liggin and Holloway, 1975).

Two additional formulations utilizing sodium naptalam are produced by Uniroyal (Dowling, 1975). The one is Nor-Crop® which mixes 8.1% (by weight) sodium naptalam with 3.0% (by weight) Chloro-IPC (Isopropyl N-(3-Chlorophenyl) Carbamate) per gallon. Another is Solo®, which also formulates Chloro-IPC with sodium naptalam. The percent by weight in the liquid formulation

is sodium naptalam 21.6% and chloro-IPC 22.2% per gallon. The granular solid formulation® mixes 10.7% sodium naptalam, 10.3% Chloro-IPC, and 79.0% inert ingredients per pound.

The liquid formulations of sodium naptalam are stored in holding tanks which dispense them to containers for shipment to customers. The containers range from 5 gallon plastic bottles and plastic-lined cans to 30 and 55 gallon drums. Shipment can also be made via railway tankers. There are no special shipping regulations other than labelling. Any mixture utilizing DNBP must be labelled a Class B Poison, due to the presence of DNBP.

3. Environmental Management

There is no waste disposal during the production of naptalam (Porter, 1975; Liggin and Holloway, 1975). From Figures V-1 and V-2, it can be seen that the entire process is carried out within a closed system. Any α-naphthylamine which does not react with the phthalic anhydride will remain dissolved in the organic solvent and be recycled to the charge tank and reactor. The α-naphthylamine contamination in the final product is discussed in Section VI-8.

The only waste which occurs, other than possible pipe or valve failure, results from the infrequent cleaning of the reactors and changing of the organic solvent. The organic solvent will need to be changed due to build-up of impurities. The solvent will contain a very small, but unknown, amount of dissolved α-naphthylamine. Reiona Chemical Co. (Liggin and Holloway, 1975) transfers cleaning wastes to settling ponds for treatment. Uniroyal and Thompson-Hayward's methods for handling cleaning wastes were not available. However, α-naphthylamine escape to the environment via this route is probably insignificant.

4. Future Manufacturers

Crystal Chemical Co. of Houston, Texas, reports (Milligan, 1973) that plans have been proposed to begin production of a herbicide called "Naphthro" in 1977. This herbicide will be very similar to the α-naphthylamine herbicides already marketed.

5. Herbicide Uses

a. Historical - Naptalam Use

Table V-2 lists annual volume of naptalam production from 1964, and the corresponding amount of α-naphthylamine used to make the naptalam.

b. Crop Protection

All three naptalam producers report (Liggin and Holloway, 1975; Fox, 1975; Dowling, 1975) that almost all production is used for pre-emergent protection of soybeans and peanuts.

The formulations containing DNBP (Dynap®, Ancrak®, NPA-1, Marauder) are applied up to the time of crop emergence for peanuts and before crop emergence for soybeans (Anon., 1974 a).

A small percentage of the naptalam produced by Uniroyal is marketed as Alanap® (Porter, 1975; Dowling, 1975). Alanap® is used in liquid formulation for control of numerous broadleaved weeds in soybeans. A 10% granular formulation is registered for use on soybeans, sweet potatoes, Irish potatoes, and vine crops (Anon., 1974 a).

Naptalam is unique because of its selective characteristics favorable to cucurbit crops, soybeans, peanuts, asparagus, sweet potatoes, and cotton. It does not kill by contact but acts rather on the seed as it germinates or through the root system. Plants that are tolerant can withstand

Table V-2. Annual Production of Naptalam, 1964-1974

	Naptalam Production (10^3 lbs)	Amount of α-Naphthylamine Used To Produce Naptalam (10^3 lbs)
1974	6000[1]	1000
1973	--	--
1972	4000	1978
1971	4332[2]	1630
1970	--	--
1969	--	--
1968	--	--
1967	--	--
1966	999[3]	490
1965	--	--
1964	1060[3]	520

[1]SRI Estimation

[2]U. S. Department of Agriculture, 1974

[3]Wheeler, 1968

a second post-emergence treatment, thereby prolonging the control (Wherry, 1968).

c. Areas of Usage

Specific crop usage and acres treated with naptalam in 1971 are listed in Table V-3, while usage by states in 1971 is listed in Table V-4.

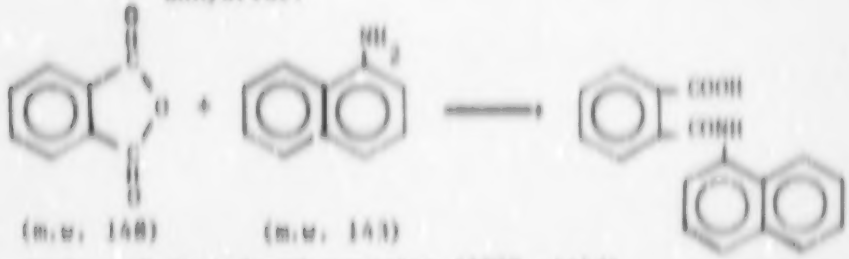
6. Economics

The following is a rough estimation of the material costs for α-naphthylamine-derived herbicide production:

Raw Materials & Cost

α-Naphthylamine	$1.10/lb	(Floyd, 1975-1976)
Phthalic Anhydride	$0.24/lb	(Chemical Marketing Reporter, 1976)
Sodium Hydroxide	$0.125/lb	

Step #1: Precipitation reaction of α-naphthylamine and phthalic anhydride:



(m.w. 148) (m.w. 143) (m.w. 291)

Basis: 1-lb-mole of naptalam (100% yield)

α-Naphthylamine	143 lb	= $157.30
Phthalic Anhydride	148 lb	= $ 35.52
		$192.82

Naptalam Cost: $192.82/291 lbs or $0.663/lb

Table V-3. Usage of Naptalam in 1971, Quantities & Acres[1]

Crop	Quantity (lb)[1] lbs Active Ingredient	Acres Treated
Soybeans	1956	1731
Peanuts	124	159
Cotton	5	17
Sorghum	3	3
Others	46	18
Total	1133	1127

[1]U. S. Department of Agriculture, 1974

Table V-4. Usage of Naptalam by States in 1971[1]

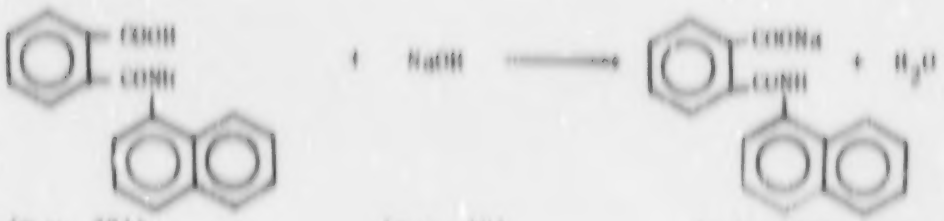
States Region[2]	Quantities (lb)[1] lbs Active Ingredient
Delta States	1783
Southeast	747
Corn Belt	587
Appalachian	173
Northern Plains	11
Southern Plains	8
Lake States	1
Total	1112

[1]U. S. Department of Agriculture, 1974

[2]See Figure V-1 for region identification

Figure V-3. Farm Production Regions

Step #2: Conversion of naptalam to sodium naptalam



(m.w. 291) (m.w. 40) (m.w. 313)

Basis: 1-lb-mole of naptalam (100% yield)

Naptalam	291 lb	= $192.82
Sodium Hydroxide	40 lb	= $ 5.00
		$197.82

Sodium Naptalam Cost: $197.82/313 lbs or $0.632/lb

This $0.63/lb is material cost only and is an approximation at best. The xylene or benzene solvent cost of $0.50 to $0.75 per gallon has not been included; however, it is reusable and is changed only periodically.

The current retail selling price of sodium naptalam (solution) is $42.00/5 gals with 2 lbs of sodium naptalam per gallon (Agway, 1975; Woolfolk Chemical Works, Inc., 1976). This makes the retail price of sodium naptalam approximately $4.20 per lb. Mark-up includes costs for labor, equipment, packaging, profits, distributors, etc.

Capital value of existing equipment was unavailable from the herbicide producers.

Most sodium naptalam is sold in formulation with the sodium salt of DNBP (sodium 4,6-dinitro-2-sec-butylphenate). DNBP is a general contact herbicide produced by the Dow Chemical Company (Anon, 1974 a). The

retail selling price of the sodium naptalam formulations (Dyanap®, Ancrak®) is currently $7.65 per gallon (Agway, 1975; Woolfolk Chemical Works, Inc., 1976). Using that price as a basis, the total sales of α-naphthylamine derived herbicides would presently be approximately $20 million. However, herbicide products are capable of having prices negotiated downwards for large volume sales (Agway, 1975; Woolfolk Chemical Works, Inc., 1976).

7. Alternative Final Use Products - Herbicides

a. Products and Usage

Table V-5 lists the quantities of naptalam used in 1971 and the major herbicides which could be used as alternatives in two large outlets for naptalam. Product chemistry and producers of these alternative herbicides are listed in Table V-6.

b. Comparative Cost and Persistence

Comparative cost to farmers and the persistence of naptalam and the major alternatives are listed in Table V-7. Table V-7 also includes the naptalam formulations of Dyanap® and Ancrak®.

Most of the naptalam is applied by farmers as Dyanap® and Ancrak®. The cost (from Table V-7) of $3-$4 per acre usage is very competitive, especially in view of the following considerations. The naptalam formulations offer a wide range of herbicide protection, including control of most broad-leaved weeds common to soybean crops. The formulations are easy to apply, can be used for both pre- and post-emergent protection on soybeans, and need not be incorporated into soil. Most of the alternatives to naptalam need to be incorporated into soil and cannot be used for post-emergent protection. For example, both these requirements apply to the relatively inexpensive linuron (Lorox®) (see Table V-7). Furthermore, it can be used only for selective weed control. Naptalam does, however, have limitations with certain soil types.

Table V-5. 1971 Use of Naptalam and Alternative Herbicides (U.S. Department of Agriculture, 1974)

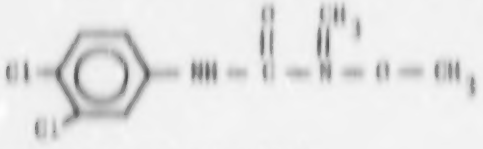
	Total U.S. Use in 1971 (10^3 lb)	Soybean Use in 1971 (10^3 lb)	Peanut Use in 1971 (10^3 lb)
Naptalam	3332	2936	324
Linuron	1803	817	--
Alachlor	14754	6304	56
Vernolate	3736	1446	2281
Amiben	9595	9340	--
Trifluralin	11427	5962	141

Table V-6. Chemistry of Alternative Products for Naptalam Applications (Spencer, 1968; Anon., 1974 a; Agway, 1975; Woolfolk Chemical Works, Inc., 1976)

1. Linuron (Lorox®)

Chemical Name: 3-(3,4-Dichlorophenyl)-1-methoxy-1-methylurea

Manufacture: Reaction of 3,4-dichlorophenyl isocyanate and N-methyl hydroxyl amine followed by methylation



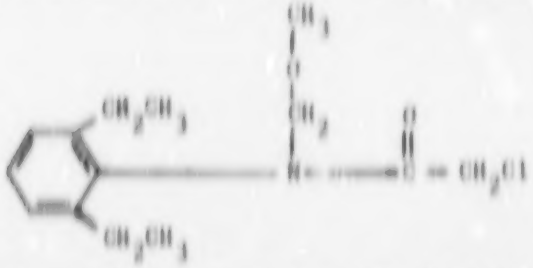
Use: Pre-emergent weed control

Formulations: Wettable power containing 50% active ingredient; Emulsifiable liquid (4 lb/gal)

Basic Producer: DuPont

2. Alachlor (Lasso®)

Chemical Name: 2-Chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide



Use: Control of annual grasses and certain broadleaf weeds. Leaves no residue in soil to carry over to next year. Can be pre-plant or surface applied. Can be mixed with Linuron for soybeans.

Formulation: 4 lb/gal Emulsifiable concentrate

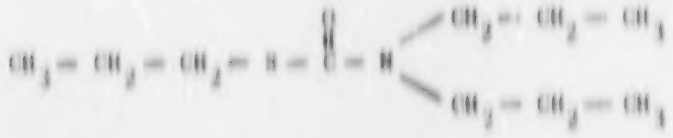
Basic Producer: Monsanto Co.

Table V-6. Chemistry of Alternative Products for Captafam Applications (Spencer, 1968; anon., 1974 a; Agway, 1975; Woolfolk Chemical Works, Inc., 1976) (Cont'd)

3. Vernolate (Vernam®)

Chemical Name: n-Propyl-di-n-propylthiolcarbamate

Manufacture: From di-propylcarbamylchloride and propyl mercaptan



Use: Control of grass weeds

Formulation: Emulsifiable liquid (6 lb/gal); Granule (10%)

Basic Producer: Stauffer Chemical Co.

4. Amiben

Chemical Name: 3-Amino-2,5-dichlorobenzoic acid

Use: Pre-emergent weed control

Formulation: Granular and liquid (2 lb/gal)

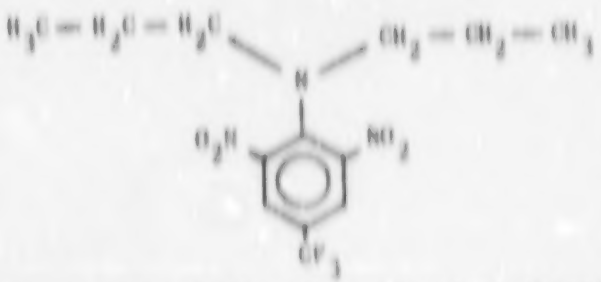
Basic Producer: Amchem Products, Inc.

Table V-6. Chemistry of Alternative Products for Captafam Applications (Spencer, 1968; Anon., 1974 a; Agway, 1975; Woolfolk Chemical Works, Inc., 1976) (Cont'd)

5. Trifluralin (Treflan®)

Chemical Name: α,α,α-Trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine

Manufacture: Reaction of 4-trifluorodinitrochlorobenzene with dipropylamine



Use: Weed control. Application made after thinning or blocking and must be incorporated in top 2 to 4 inches of soil immediately. Will not control established weeds.

Formulation: Emulsifiable concentrate (4 lb/gal)
Granular 5%

Basic Producer: Elanco Products Co., division of Eli Lilly and Co.

Table V-7. Alternative Herbicide Products--Comparative Cost and Persistence

	Current Retail[1] Selling Price/Unit	Approximate Cost to Farmer Per Acre Use[2]	Persistence[3] Time in Months for 75-100% Disappearance
Naptalam[4]	$8.40/gal	$4-$5	1-3
Linuron	$3.70/lb	$1½-$2½	1-10
Alachlor	$15.00/gal	$4-$5	1-3
Vernolate	$17.95/gal	$7-$8	1-3
Amiben	$11.10/gal	$5-$6	1-3
Trifluralin	$31.20/gal	$5-$6	1-3
Dyanap®	$7.65/gal	$3-$4	1-3
Ancrak®	$7.65/gal	$3-$4	1-3

[1] Agway (1975); Woolfolk Chemical Works, Inc. (1975)

[2] Calculated from data from U. S. Department of Agriculture (1974); Agway (1975); and Woodfolk Chemical Works, Inc. (1976)

[3] Von Rumker et al. (1974)

[4] Current price for Alanap®

a. Dyes

1. Processing Sites

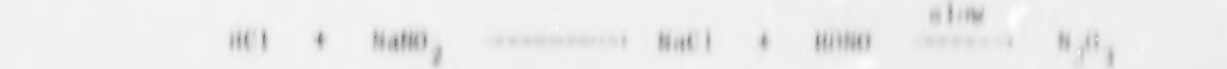
α-Naphthylamine-derived dye processing sites are listed in Table V-8 by company, products, and estimated annual production.

2. Process Description

The general method for dye production incorporating α-naphthylamine is illustrated in Figure V-4.

The diazotization reaction occurs in a batch reactor made of either wood or coated metal. The most convenient solvent for the diazotization is water, which is used whenever possible (Thomaidson, 1958), as is the case with α-naphthylamine.

The initial amine chemical intermediate (usually not α-naphthylamine) is dissolved in water, usually as the hydrochloride, and introduced into the reactor where it is cooled to 0°C by addition of crushed ice while hydrochloric acid is slowly added. To the resulting solution or suspension, a solution of sodium nitrite is rapidly injected under the surface and reacts with a portion of the hydrochloric acid to form nitrous acid:



The nitrous acid diazotizes the initial chemical intermediate by the following proposed mechanism (March, 1968):

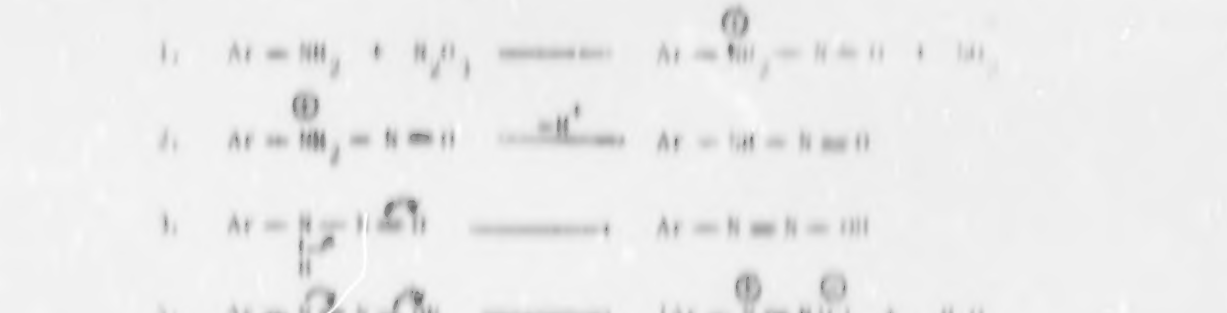


Table V-6. Processing Sites for 4-Aminobiphenyl Dyes

Company	Site	Products[1]		Estimated Annual[2] Dye Production, Active Ingredients	Capacities
1. American Color & Chemical Co.	Reading, PA	Acid Orange	116	<2 Million lbs	N.A.
		Acid Blue	113		
		Acid Black	24		
		Direct Blue	71		
		Direct Blue	70		
		Disperse Black	1		
2. Crompton & Knowles Corp.	Gibraltar, PA	Acid Blue	113	<2 Million lbs	N.A.
		Direct Blue	70		
		Disperse Black	1		
		Others (Classified Structures)			
3. GAF Corp.	Reasonlawn, NY	Acid Orange	116	<½ Million lbs	N.A.
		Acid Blue	113		
		Acid Black	24		
		Disperse Black	1		
4. Harshaw Chemical Co., Div. of Kewanee Ind Co.	Louisville, KY Lowell, NC	Pigment Red	54	<50,000 lbs	N.A.
		Direct Blue	124	<50,000 lbs	

[1] For chemical structures, see Table V-23

[2] 1981 Estimation

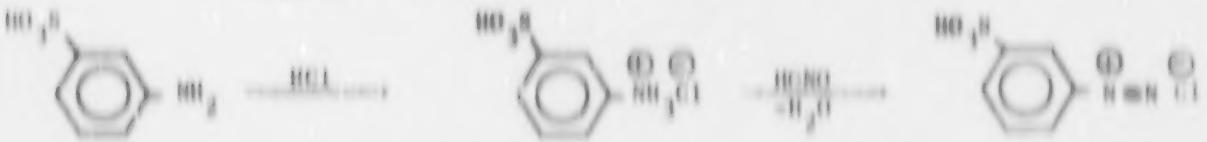
Figure 7-4. Dye Process Schematic (adapted from information from Donaldson, 1978; various personal communications)

sufficient hydrochloric acid has been previously added to insure formation of the diazonium chloride ($Ar\text{-}\overset{+}{N}\equiv N\ \overset{-}{Cl}$). Tests are conducted to make sure diazotization is completed.

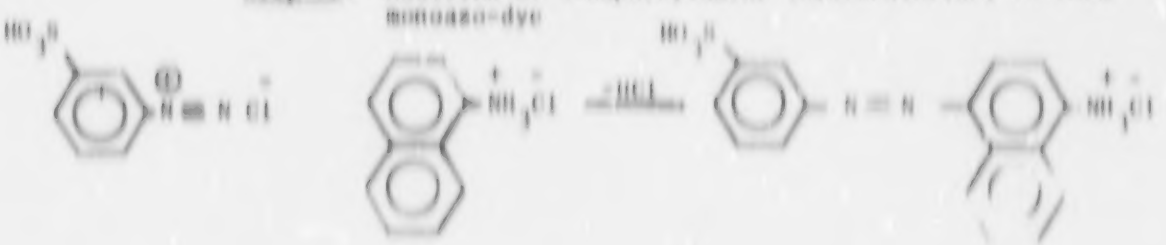
The α-naphthylamine is converted to the more water soluble hydrochloride salt prior to addition to the reactor by dissolving it in boiling water containing hydrochloric acid. This solution is allowed to cool to 50°C and is then charged into the reactor at a rate determined by previous experience. Crushed ice is periodically added to maintain a temperature range of 0°-5°C in the reactor to prevent decomposition of the diazonium chloride. When the coupling reaction is complete, the diazonium chloride and α-naphthylamine will form a monoazo-dye. If another chemical intermediate is to be coupled to this monoazo-dye, which is usually the case, hydrochloric acid and sodium nitrite are added to diazotize the monoazo-dye, and the process proceeds as previously described. The entire process may take several days to complete (Allied Chemical Corp., 1975).

As an example, consider Acid Blue 113, which is the largest volume α-naphthylamine-derived dye produced in the United States:

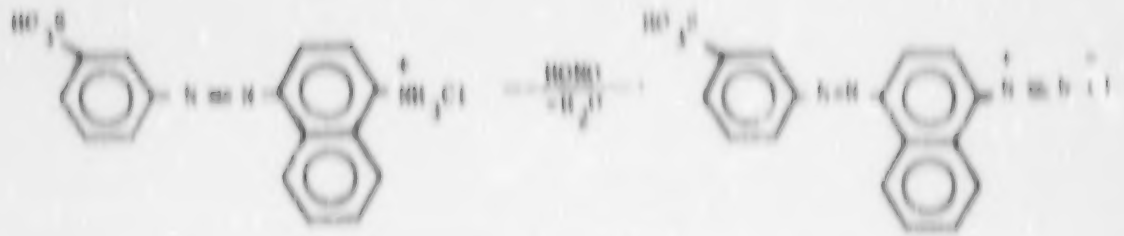
Step #1: Diazotization of metanilic acid



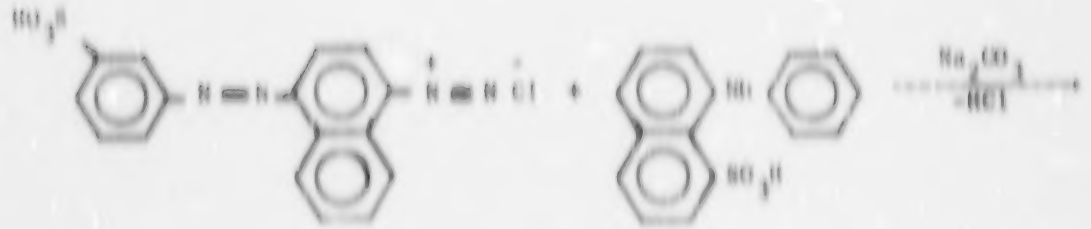
Step #2: Addition of α-naphthylamine (hydrochloride) to form monoazo-dye

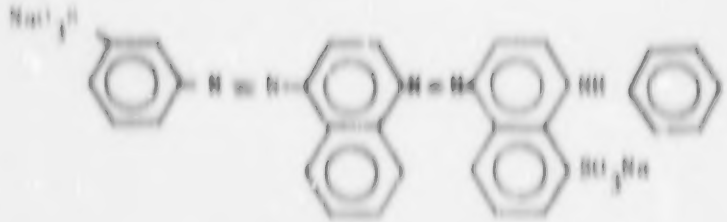


Step (3): Diazotisation of monoazo-dye



Step (4): Addition of N-phenyl Peri acid and neutralisation to form Acid Blue 113





(Acid Blue 113)

Sodium carbonate is added to the reactor to neutralise any excess acid. The dye, which is water soluble, is now "salted-out" (precipitated-out) of solution by addition of sodium chloride. This "mother liquor" is now transferred from the reactor to filter presses to remove the excess water and to collect the solid dye. The excess water goes to waste disposal while the "filter cakes" (the solid dyes) are thoroughly dried in ovens and then granulated by mechanical means to the required mean sizes.

The granulated dye is taken to the packaging department and "cut" to commercial strength by additions of sodium sulfate, non-dusting agents, surfactants, dextrins, and other inert ingredients. The actual dye content of the final product may be as low as 25% (Rounds, 1975).

The commercial strength dye is packaged into common fiberboard drums for shipment to customers. There are no shipping regulations or required safety precautions during shipment of any α-naphthylamine-derived dyes.

3. Environmental Management

Effluents from α-naphthylamine dye production that need to be disposed of originate at the filter pressing stage as shown in Figure V-4. At this stage, the "mother liquor" is forced against filter cloth which separates the dye solids from the excess liquid. This excess liquid will mainly be a saline solution, but it will also contain small amounts of dye, unreacted intermediates, and possibly some excess acid. After adjusting the pH, the excess liquid is released to city or county sewage systems or to the ocean. Disposal methods used by the current manufacturers are listed in Table V-9. The disposed dye and unreacted intermediates will be discussed in Section VI-C (Material Balance - Exposure to the Environment).

4. Use

Table V-10 lists the quantities of α-naphthylamine used for domestic dye production for 1964-1973. The production quantities and prices of the individual α-naphthylamine derived dyes for 1964-1973 are listed in Table V-11. Table V-12 lists the companies and the α-naphthylamine dyes they produced from 1964-1973.

Table V-6. Disposal of Dye Wastes

Manufacturer	Site	EPA Region	Disposal
1. American Color & Chemical Co.	Reading, PA	III	City or county sewage system
2. GAF Corp.	Rensselaer, NY	II	City or county sewage system
3. Crompton & Knowles Corp.	Ciba-Geigy, PA	III	To the ocean[1]
4. Hercules Chemical Co.	Louisville, KY	IV	City or county sewage system
Div. of Kenmore Mill Co.	Lowell, NC	IV	City or county sewage system

[1]Alternative disposal methods are being evaluated (Benning, 1977)

Table V-10. Annual Consumption of α-Naphthylamine Used in Dye Production

Year	Quantity (10^3 lb)[1]
1973	840
1972	910
1971	840
1970	690
1969	720
1968	690
1967	450
1966	570
1965	620
1964	610

[1]NRC Estimation

Table V-11. Dyes Made Directly from α-Naphthylamine (U.S. International Trade Commission, 1969-1973)

Reproduced from best available copy.

Table V-12. α-Naphthylamine Dye Producers and Products, 1964-1973
(U.S. International Trade Commission, 1960-1973; Anon., 1974 b)

Note: Parenthesized years indicate production years; all = 1964-1973.
* Indicates no longer manufacturing α-naphthylamine dyes.

1. *Allied Chemical--Specialty Chemicals Div.; Buffalo, NY
   - Acid Orange 116 (all)
   - Acid Blue 113 (1966-1973)
   - Acid Blue 120 (all)
   - Acid Black 24 (all)
   - Acid Red 17 (all)
   - Direct Blue 71 (all)
   - Direct Blue 78 (all)
   - Direct Blue 126 (1964-1967)
   - Solvent Black 1 (all)

2. American Color & Chemical Corp.; Lock Haven, PA
   (American Aniline Products)
   - Disperse Black 1 (all)

3. *Atlantic Chemical Corp.; Nutley, NJ
   - Acid Orange 116 (1965, 69, 73)
   - Acid Blue 113 (1966-1973)
   - Acid Blue 120 (1969-1973)
   - Acid Black 268 (1970-1973)
   - Acid Red 17 (all)
   - Azoic Coupling Component 4 (1964, 66, 67, 69-73)
   - Direct Blue 71 (1964, 65, 69-73)
   - Direct Blue 78 (all)
   - Direct Blue 81 (all)
   - Direct Blue 126 (1969-1973)
   - Direct Red 7 (1966-1973)

4. *Baychem Corp.; Bayonne, NJ
   - Acid Orange 116 (1972)
   - Direct Blue 71 (1971)
   - Direct Blue 126 (all)

5. *Benzenoid Organics, Inc.; Bellingham, MA
   - Acid Blue 113 (1965-1973)

6. *Bernacolors-Poughkeepsie Inc.; Poughkeepsie, NY
   - Acid Blue 113 (1969-1973)

7. *Blackman-Uhler Chemical Co.; Spartanburg, SC
   - Azoic Coupling Component 4 (all)

8. Crompton & Knowles Corp.; Gibraltar, PA
   - Acid Orange 116 (1965-1973)
   - Acid Blue 113 (1967-1973)

9. *E. I. duPont; Deepwater Point, NJ
   - Acid Blue 113 (all)
   - Acid Black 24 (all)
   - Acid Black 268 (all)
   - Disperse Black 1 (all)
   - Direct Blue 71 (1964-1968)
   - Direct Blue 78 (all)
   - Direct Blue 126 (1964-1968)

Table V-12: β-Naphthylamine Dye Producers and Products, 1964-1973
U.S. International Trade Commission, 1960-1972; Anon., 1974 b)
(cont'd)

10. *Fabricolor Inc.; Paterson, NJ
Acid Orange 116 (1968-1973)
Acid Blue 113 (1968-1973)

11. GAF Corp.; Rensselaer, NY
Acid Orange 116 (1966-1973) Direct Blue 71 (all)
Acid Blue 113 (all) Direct Blue 78 (1965-1967)
Acid Blue 120 (all) Direct Blue 126 (1968-1968)
Acid Black 24 (all) Disperse Black 1 (all)
Acid Black 268 (1973)
Azoic Coupling Component 4 (1964-1973)

12. Harshaw Chemical Co.; Louisville, KY
Pigment Red 54 (all)

13. *Hercules, Inc.; Glens Falls, NY
Pigment Red 54 (all)

14. *Hilo Mars Color & Chemical Co.; Irvington, NJ
Pigment Red 54 (1964-1967)

15. *Keystone Inc.; Ashland, MA
Acid Orange 116 (1972-1973) Acid Black 24 (1964-1971)
Acid Blue 113 (all) Direct Blue 78 (all)

16. *Printex Chemical Inc.; Charlotte, NC
Azoic Coupling Component 4 (1965-1970)

17. *Sterling Drug, Inc. (Hilton-Davis Chemical); Cincinnati, OH
Pigment Red 54 (all)

18. *Tennaco Inc.; Reading, PA
Acid Orange 116 (1964, [illegible], 73)
Acid Blue 113 (1965-1973)
Acid Blue 120 (1964)

19. *Toms River Chemical Corp.; Toms River, NJ
Acid Orange 116 (all) Direct Blue 71 (all)
Acid Blue 113 (1967-1973) Direct Blue 78 (all)
Acid Black 268 (1964-1972) Direct Blue 126 (all)
Acid Red 17 (all) Disperse Black 1 (all)

20. H. H. Young (Young's Aniline Works); Baltimore, MD
Acid Orange 116 (1969-1973)
Acid Blue 113 (1970-1973)
Acid Red 17 (1964-1969)

Table V-12. 1-Naphthylamine Dye Producers and Products, 1964-1973 (U.S. International Trade Commission, 1960-1973; Anon., 1974 b) (Cont'd)

21. *John Campbell & Co.; Perkasie, PA					
Acid Blue	111	(to 1973)	Direct Blue	71	(to 1973)
Acid Black	24	(to 1973)	Direct Blue	78	(to 1973)
Acid Red	17	(to 1973)			
22. *Sandoz-Wander, Inc.; Hanover, NJ					
Acid Orange	116	(to 1973)	Acid Black	36A	(to 1973)
Acid Blue	111	(to 1973)	Direct Blue	71	(to 1973)
Acid Red	17	(to 1973)	Direct Blue	78	(to 1973)
Acid Blue	120	(to 1973)	Direct Blue	126	(to 1973)
23. *Organic Chemical Corp.; E. Providence, RI					
Acid Blue	111	(to 1973)			
24. *ICI America, Inc; Dighton, MA					
Acid Blue	111	(to 1973)			

Table V-13 contains information on the individual α-naphthylamine-derived dyes such as estimated current annual production, chemical formula, raw materials and synthesis approaches, and current producers.

5. Economics

The following is a rough estimation of the material costs of the major intermediates used in α-naphthylamine-derived dye production (Chemical Marketing Reporter, 1976; various personal communications):

α-Naphthylamine (flaked)	$1.45/lb
Metanilic Acid	$1.35/lb
N-Phenyl-Peri Acid	$1.35/lb
p-Cresol	$0.72/lb
5-Amino-1-Naphthalenesulfonic Acid	$0.87/lb
1,7-Cleve's Acid	$2.42/lb
J Acid (6-Amino-1-naphthol-3-sulfonic acid)	$4.72/lb
N-Phenyl-J Acid	$4.72/lb
p-Nitroaniline	$0.84/lb
1-Naphthol-5-Sulfonic Acid	$2.25/lb
Sodium Nitrite	$0.19/lb
Hydrochloric Acid	$0.22/lb

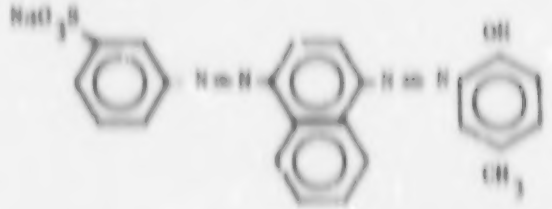
Consider Acid Blue 113 (Metanilic Acid ——→ α-Naphthylamine ——→ N-Phenyl-Peri Acid). The raw material costs amount to approximately $2.70 per pound of Acid Blue 113. However, the 100% strength dye is "cut" to commercial strength by addition of inert ingredients such as sodium sulfate and dextrins. This enables the dye purchasers to more accurately weigh-out a specific strength of dyes, and at the same time, aid the dyeing

Table V-13. Dyes Manufactured from α-Naphthylamine (Anon., 1974 b; Colour Index; various personal communications)

1. Acid Orange 116

Estimated Annual Production: <1 million pounds

Chemical Formula:



Raw Materials: Metanilic Acid ——— α-Naphthylamine ——— p-Cresol

Current Producers and Tradenames:
GAF Corp. - Nylitan Fast Orange DNL
American Color & Chemical Co. - Duromyl Fast Orange LEF

2. Acid Blue 113

Estimated Annual Production: <1 million pounds

Chemical Formula:

Raw Materials: Metanilic Acid ——— α-Naphthylamine ——— N-Phenyl Peri Acid

Current Producers and Tradenames:
Crompton & Knowles Corp. - Intrazone Blue 3R
GAF Corp. - Sulpho Cyanine 5RA or Funaso Blue 5RA
American Color & Chemical Co. - Amacid Cyanine 5RA

Table V-13. Dyes Manufactured from α-Naphthylamine (Anon., 1974 b; Colour Index; various personal communications) (Cont'd)

4. Acid Black 26

Estimated Annual Production: <100,000 pounds

Chemical Formula:

Raw Materials: 5-Amino-1-Naphthalenesulfonic Acid ——— α-Naphthylamine ——— N-Phenyl Peri Acid

Current Producers and Tradenames:
GAF Corp. - Sulphon Cyanine Black BA
American Color & Chemical Co. - Duracol Milling Black B

5. Acid Black 26A

Chemical Formula:

Raw Materials: 5-Amino-2-(o-toluido)-benzenesulfonic Acid ———
α-Naphthylamine ——— 2-Hydroxy-6-naphthalenesulfonic Acid (Schaeffer's Acid)

Current Producers: None

Table V-13. Dyes Manufactured from α-Naphthylamine (Anon., 1974 b; Colour Index; various personal communications) (Cont'd)

5. Acid Blue 120

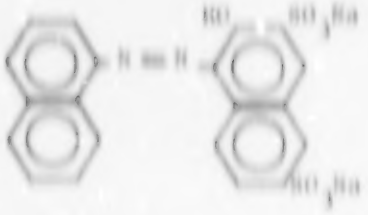
Chemical Formula:

Raw Materials: Metanilic Acid → α-Naphthylamine → N-p-Tolyl Peri Acid

Current Producers: None

6. Acid Red 17

Chemical Formula:



Raw Materials: α-Naphthylamine → 1-Hydroxy-2,7-Naphthalenedisulfonic Acid (R Acid)

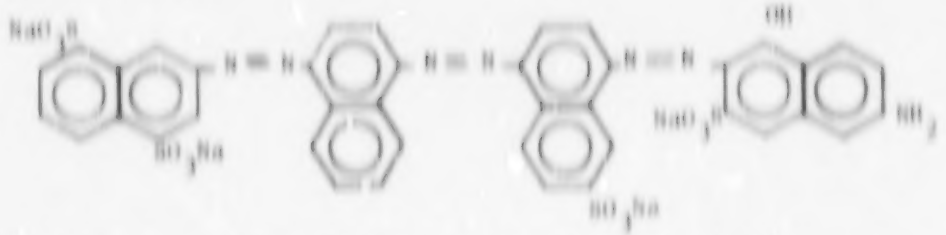
Current Producers: None

Table V-13. Dyes Manufactured from α-Naphthylamine (Anon., 1974 b; Colour Index; various personal communications) (Cont'd)

7. Direct Blue 71

Estimated Annual Production: Not Available

Chemical Formula:



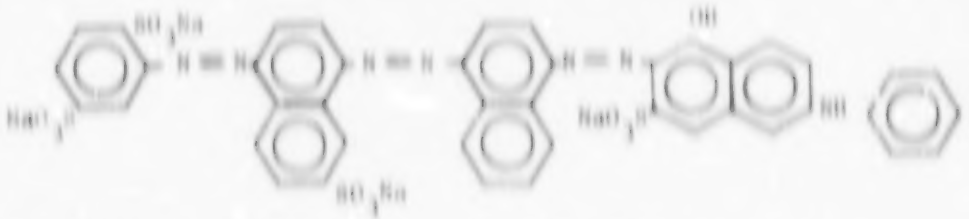
Raw Materials: 3-Amino-1,5-Naphthalenedisulfonic Acid → α-Naphthylamine → 1,7-Cleve's Acid → 6-Amino-1-Naphthol-3-Sulfonic Acid (J Acid)

Current Producer and Tradename:
American Color & Chemical Co. - Amanil Fast Blue FFB

8. Direct Blue 78

Estimated Annual Production: Not Available

Chemical Formula:



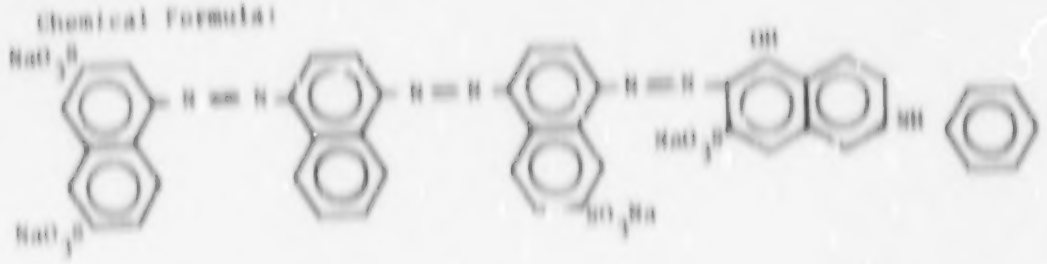
Raw Materials: 2-Amino-p-benzenedisulfonic Acid → 1,7-Cleve's Acid → α-Naphthylamine → 8-Phenyl J Acid

Current Producers and Tradenames:
American Color & Chemical Co. - Amanil Fast Blue 4GL
Crompton & Knowles Corp. - Intralite Blue 4GL New

Table V-11. Dyes Manufactured from α-Naphthylamine (Anon., 1974 b; Colour Index; various personal communications) (Cont'd)

9. Direct Blue 81

Chemical Formula:



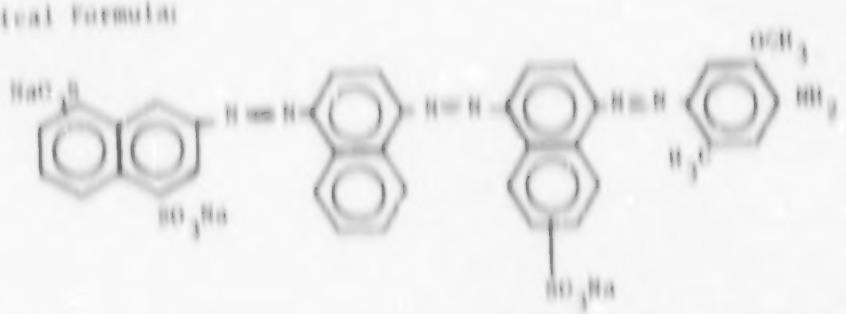
Raw Materials: p-Phenylsulfonyl H Acid ——— α-Naphthylamine ——— 1,7-Cleve's Acid ——— N-Phenyl J Acid

Current Producers: None

10. Direct Blue 126

Estimated Annual Production: >100,000 pounds

Chemical Formula:



Raw Materials: 4-Amino-1,5-Naphthalenedisulfonic Acid ——— α-Naphthylamine ——— 1,6-(and 1,7)-Cleve's Acid ——— Cresidine

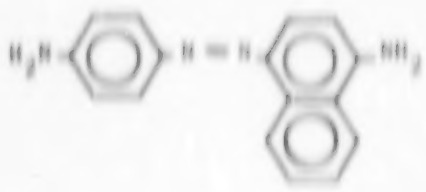
Current Producer and Tradename:
Harshaw Chemical Co. - Helamine Diazo Blue 2BW 200% New

Table V-11. Dyes Manufactured from α-Naphthylamine (Anon., 1975 b; Colour Index; various personal communications) (Cont'd)

11. Disperse Black 1

Estimated Anaual Production: Not Available

Chemical Formula:



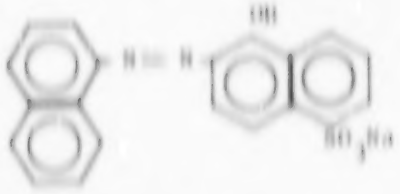
Raw Materials: p-Nitroaniline (NO_2 group reduced after diazotization)
α-Naphthylamine

Current Producers and Tradenames:
American Color & Chemical Co. - Amacel Black AS Ext.
GAF Corp. - Cellitazol BBD Extra
Crompton & Knowles Corp. - Intrasperse Diazo Black GNSP

12. Pigment Red 38

Estimated Annual Production: >100,000 pounds

Chemical Formula:



Raw Materials: α-Naphthylamine → 1-Naphthol-5-Sulfonic Acid

Current Producer and Tradename:
Harshaw Chemical Co. - Harmon BB Toner 1159

Table V-13. Dyes Manufactured from α-Naphthylamine (Anon., 1975 b; Colour Index; various personal communications) (Cont'd)

13. Solvent Black 3

Chemical Formula:

Raw Materials: Aniline ⟶ α-Naphthylamine ⟶ 3,3-Dihydr-2,2-Dimethylperimidine

Current Producers: None

14. Azoic Coupling Component No. 4

Chemical Formula:

Raw Materials: α-Naphthylamine ⟶ 3-Hydroxy-2-Naphthoic Acid

Current Producers: None

process. Addition of these inert ingredients varies from dye to dye and from manufacturer to manufacturer. The retail selling price of commercial strength Acid Blue 113 is approximately $3.60/lb (Chemical Marketing Reporter, 1976).

It is impractical to attempt to evaluate costs considering the unknown additions of inert ingredients. However, in 1973 total sales from α-naphthylamine-derived dyes amounted to approximately $5 million (calculated from data from United States International Trade Commission, 1960-1973).

b. Alternative Final Use Products - Dyes

Each organic dye has a different chemical formula and a different hue. This means that Acid Blue 113, for example, will have a different hue from all the other Acid Blues. Also, the unique chemical formula of each dye gives it individual dyeing properties such as fastness, dischargeability, effect on metal, and fiber suitability.

It may be possible, however, to imitate the hue of a dye by mixing combinations of other dyes. For example, the hue of Acid Blue 113 may possibly be obtained by mixing other Acid Blues with other Acid colors. This mixing technique makes it theoretically possible to obtain any α-naphthylamine dye hue, regardless if the dye is Acid, Direct, Disperse, or any other dye grouping. The major problem would be the suitability of the mixed dye. It may not have the essential properties for coloration inherent in the α-naphthylamine dye. This would have to be ascertained by experimentation.

In general, specific alternatives to α-naphthylamine dyes have not been developed because the need has never existed. An exception is an Acid Orange 116 product offered for sale by Hyman Inc. The Hyman product does not use α-naphthylamine. This will be discussed further in the next section.

7. Alternative Chemicals for Synthesis

A number of dye producers have indicated efforts to synthesize α-naphthylamine dye formulas with intermediates other than α-naphthylamine. All but one dye producer report that the efforts have been unsuccessful as the new synthesis made a very inferior dye. The exception is Nyanza Inc. (Leary, 1975). Nyanza has synthesized an Acid Orange 116 without the use of α-naphthylamine. The process is considered proprietary information and, therefore, was not available. It should be noted, however, that Nyanza's Acid Orange 116 is slightly more expensive than the α-naphthylamine Acid Orange 116 and has some restrictions for use in continuous dyeing operations. However, it does indicate the possibility of synthesis without α-naphthylamine.

C. Discontinued Uses

1. Substituted α-Naphthylamine Derivatives

In the past, α-naphtaylamine has been used to synthesize a number of chemical intermediates. Domestically, however, α-naphthylamine is no longer used for these synthesis applications. These applications have either been terminated or replaced with a substitute process which does not utilize α-naphthylamine.

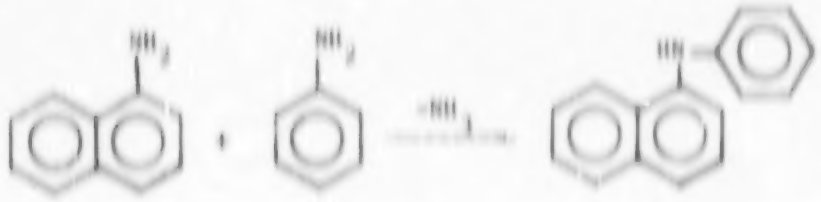
Table V-14 lists the 1972 production volumes and values of α-naphthylamine-derived intermediates for DuPont, the only producer in 1972. Additional information concerning the derived intermediates is given below.

Table V-14. 1972 DuPont Production Quantities and Values for α-Naphthylamine Derived Intermediates

Intermediates	Production Quantities (10^3 lbs)	Value (10^3 $)
N-Ethyl-α-Naphthylamine	276	290
Sodium Naphthionate	1,100	770
N-Phenyl-α-Naphthylamine	2,557	1,760
β-Naphthionic Acid	15	67
1-Naphthol-6-Sulfonic Acid (Cleve and Winther's Acid)	71	110

a. N-Phenyl-α-Naphthylamine

N-Phenyl-α-naphthylamine is still being domestically produced, but not from α-naphthylamine. The terminated α-naphthylamine process involved vapor phase condensation of α-naphthylamine with aniline over alumina gel at 400°C or fractional distillation of heated α-naphthylamine, aniline, and catalyst (p-toluenesulfonic acid) (Donaldson, 1958). The production chemistry was:



This was the method employed by DuPont up through 1973; at that time DuPont switched to an alternative method, not using α-naphthylamine. Union Carbide has also produced N-phenyl-α-naphthylamine (1967, 1968, 1972, 1973) (U.S. International Trade Commission, 1960-1973), however the Carbide process probably utilized the Bucherer reaction described below.

In the alternative production method, α-naphthol is reacted with aniline. The α-naphthol hydroxyl group is replaced by an amino group from the aniline (or aniline sulfite can be used) in the presence of ammonium sulfite catalyst, and is known as the Bucherer reaction (Bent, 1963). The suggested mechanism is illustrated below:

N-Phenyl-α-naphthylamine is used as an antioxidant for rubber, petroleum, paint, and plastic. The less expensive cost of α-naphthol ($0.75/lb) (Chemical Marketing Reporter, 1975), compared to α-naphthylamine ($1.10/lb), makes the substitute process economically more favorable.

b. N-Ethyl-α-Naphthylamine

N-Ethyl-α-naphthylamine is still being domestically produced by DuPont, but not using α-naphthylamine. The terminated process involved heating α-naphthylamine with ethyl chloride.

In addition to DuPont, Dye Specialties, Inc. has produced N-ethyl-α-naphthylamine (1966-1969, 1967-1969, 1971-1973) (U.S. International Trade Commission, 1960-1973). The Dye Specialties process method was not available; however, use was probably captive for dye production. The only major use for N-ethyl-α-naphthylamine is as a dye intermediate.

A possible alternative production method again involves the Bucherer reaction of α-napthol and ethylamine in the presence of ammonium bisulfite.

Comparative raw material cost would be as follows (Boyd, 1975-1976; Chemical Marketing Reporter, 1976):

α-naphthylamine	$1.10/lb	α-napthol	$0.75/lb
ethyl chloride	$ .09/lb	ethylamine	$0.49/lb

α-Naphthylamine Process: $0.95/lb raw material cost

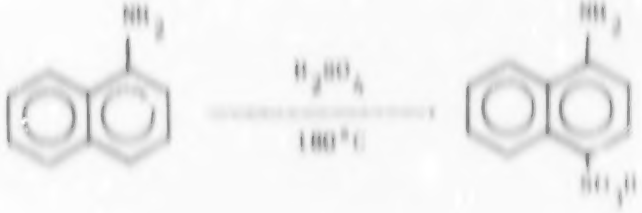
α-Naphthol Process: $0.78/lb raw material cost

Here again, the substitute process is economically more favorable.

c. Sodium Naphthionate (Naphthionic Acid-Sodium Salt)

Sodium naphthionate or naphthionic acid is no longer made in the United States. Approximately 2.5 million lbs of these chemicals are used annually for dye production (SRC estimation). The only present source for the dye producers is importation. Past domestic producers of sodium naphthionate and naphthionic acid, from 1964, include DuPont (1964-1973), Allied Chemical (1964-1970), and American Cyanamid (1964-1973) (U.S. International Trade Commission, 1960-1973).

The naphthionic acid was prepared by sulfonation of α-naphthylamine. α-Naphthylamine, direct from its purification process, is run (in molten form) to a reactor containing an equimolar amount of concentrated sulfuric acid (Allied Chemical Corp., 1975).



Neutralization with caustic soda or soda ash gives the sodium naphthionate. There is no known practical method for producing naphthionic acid without using α-naphthylamine. Estimates of historical production quantities for sodium naphthionate are given in Table V-15, along with the isolated quantities of naphthionic acid not neutralized to the sodium salt.

d. 1-Naphthol-4-Sulfonic Acid (Neville and Winther's Acid)

1-Naphthol-4-sulfonic acid is no longer made in the United States. However, it is currently used as a dye intermediate, with annual use nearing 200,000 lbs (SRI estimation), all of which is presently imported. In the past, DuPont (1964-1973) and Allied Chemical (1964-1970) produced the acid in quantities approaching one-half the total domestic consumption (see Table V-16 for 1-naphthol-4-sulfonic acid production estimates).

1-Naphthol-4-sulfonic acid was prepared by the Bucherer reaction by heating naphthionic acid with sodium bisulfite liquor at 90-100°C and treating the resulting intermediate with sodium hydroxide.

There is no known practical method for preparing 1-naphthol-4-sulfonic acid without using α-naphthylamine derivatives. The direct sulfonation of 1-naphthol results in a mixture of the 2- and 4-isomers (Treibs, 1967).

Table V-15. Annual Production Quantities of Sodium Naphthionate and Naphthionic Acid

Year	Production Quantities[1] of Sodium Naphthionate (10^3 lb)	Production Quantities[2] of Isolated Naphthionic Acid (10^3 lb)
1973	1400	***
1972	1 800	***
1971	1350	***
1970	1450	***
1969	750	178
1968	650	173
1967	1150	141
1966	***	225
1965	***	149

[1]SRI Estimations

[2]U.S. International Trade Commission (1960-1973)

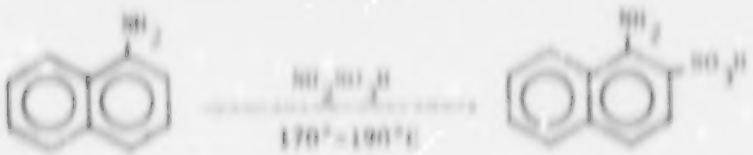
Table V-16. Annual Production Quantities of 1-Naphthol-4-Sulfonic Acid[1]

Year	10^3 lb
1973	***
1972	71
1971	110
1970	105
1969	90
1968	90
1967	160

[1]SRI Estimations

c. β-Naphthionic Acid

β-Naphthionic acid is no longer produced in the United States. DuPont was the only domestic producer after 1964; production years 1964-1973 (U.S. International Trade Commission, 1966-1973). β-Naphthionic acid was used in pigment production. It was manufactured by heating α-naphthylamine with sulfuric acid at 180-185°C, or with aminosulfonic acids at 170-190°C (Donaldson, 1958; Treibs, 1967).



there is no practical method for production without using α-naphthylamine derivatives.

d. Aldol-α-Naphthylamine Condensate

In 1973, B.F. Goodrich Co., Chemicals Division, Akron, Ohio, terminated production of a rubber antioxidant called aldol-α-naphthylamine condensate. For production, α-naphthylamine was reacted with aldol (3-hydroxybutanol); the details of the process were not available. Reaction chemistry was probably the following:

Approximately 200,000 lbs of aldol-α-naphthylamine condensate were produced in 1972 (SRI estimation).

3. Rodenticide (α-Naphthylthiourea)

In 1973, U.S. Patent and Co., division of IPC International, Inc., terminated production of the rodenticide α-naphthylthiourea, tradenamed ANTU. α-Naphthylthiourea is manufactured by the interaction of α-naphthylamine and ammonium thiocyanate (Spencer, 1968).

α-Naphthylthiourea is a rat poison specific to the Norway rat with toxic doses of 6-8 mg/kg. It is less toxic to other species of rat and is relatively harmless to man and herbivores. It will induce vomiting in dogs. Formulation consists of baits of 1-3% in suitable protein or carbohydrate-rich material. It is chemically stable on exposure to air and sun (Spencer, 1968).

α-Naphthylthiourea is presently being imported by the Mallinckrodt Chemical Co. in very small quantities with prices ranging from $3.25/lb to $4.50/lb (Kaner, 1975). Import history is listed below (U.S. Dept. of Agriculture, 1971):

Year	Quantity in Pounds
1967	5,676
1968	1,617
1967	2,000
1966	5,000
1965	6,500

There is no practical method for producing α-naphthylthiourea without α-naphthylamine. However, there are excellent alternatives to α-naphthylthiourea use in rodent control, notably, Warfarin.

VI. Material Balance - Exposure to the Environment

This section considers the possible release and exposure of α-naphthylamine to man and the environment. Occupational exposure to persons involved in the production and use of α-naphthylamine is regulated by OSHA standards (Appendix A) as of January 29, 1974, and will not be considered.

A. α-Naphthylamine Manufacture

There appears to be no disposal or loss of α-naphthylamine to the environment during the manufacturing process used for α-naphthylamine. Any wastes or by-products generated during the process are collected and incinerated. Cleaning wastes are also incinerated (Boyd, 1975-1976). After formation, the chemical is shipped and stored in the molten form. It is possible that small spills or leaks from the equipment could occur, but OSHA standards and the manufacturer (Boyd, 1975-1976) suggest that any wastes from the cleanup of such spills would be incinerated and not be released to the external environment.

B. Herbicides

There appears to be no disposal or loss of α-naphthylamine to the environment during the manufacturing process for herbicides. Small quantities of α-naphthylamine may be released when the reactors are cleaned or pipes and valves fail, but these quantities are probably insignificant.

The only potential route for significant α-naphthylamine exposure to the environment from α-naphthylamine-derived herbicides is from the final herbicide products. In the manufacturing process the α-naphthylamine and phthalic anhydride have been dissolved in the xylene, benzene, or kerosene and react to form naptalam which precipitates out of solution. The reaction is at least

99% complete by the time the naptalam leaves the reactor for separation (Porter, 1975). In order for the unreacted α-naphthylamine to contaminate the final product, it must either be extracted by the sodium salt solution or be retained on the filtered naptalam, depending upon the separation method used.

It appears highly unlikely that the unreacted α-naphthylamine will be extracted from the benzene or xylene solution into the aqueous sodium hydroxide solution. α-Naphthylamine is very soluble in xylene or benzene but fairly insoluble in water (0.469 g/l). Naptalam is soluble in the basic aqueous solution because it can form the water-soluble sodium salt of the phthalamic acid. However, α-naphthylamine is a weak base and therefore would not disassociate and be extracted into the aqueous sodium hydroxide solution.

If the naptalam is separated from the organic solvent by filtration, some unreacted α-naphthylamine might remain on the filter cake. Since the reaction is 99% complete and α-naphthylamine is very soluble in benzene or xylene, the amount of α-naphthylamine remaining in the naptalam or sodium naptalam product should be extremely small. No analytical study could be located which had attempted to measure the concentration of α-naphthylamine in the naptalam.

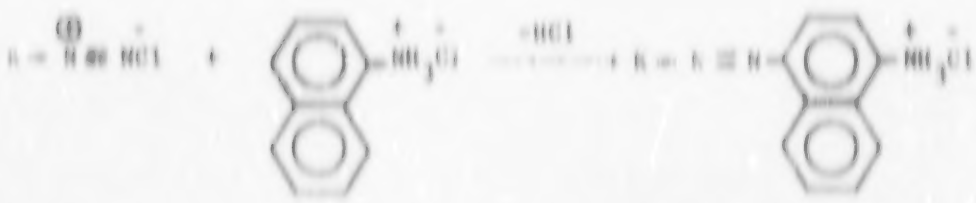
Naptalam is susceptible to hydrolysis at pH 9.1 or higher, which would result in the formation of α-naphthylamine and phthalic acid. However, the aqueous solutions of the sodium naptalam are very stable, since the pH is close to neutral.

E. Dyes

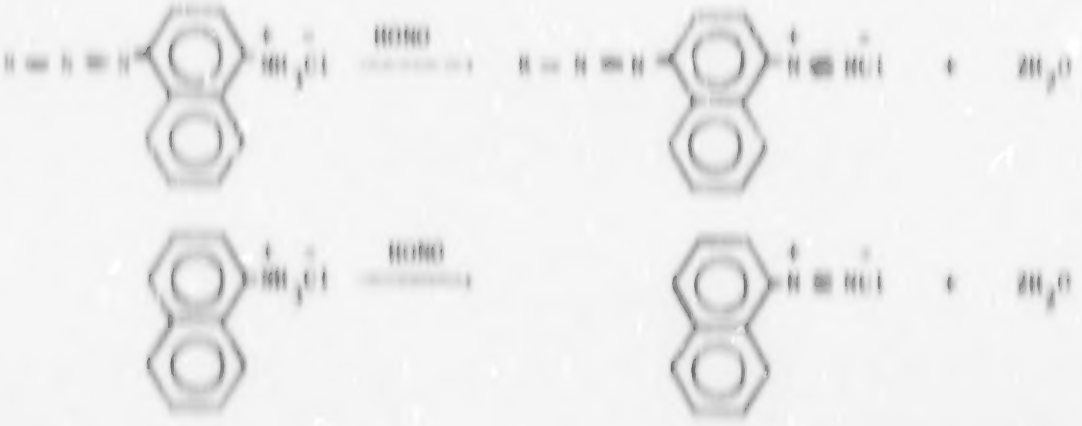
The percent yield for the reactions used to produce α-naphthylamine-derived dyes, like most organic reactions, rarely exceeds 95%. This will vary from dye to dye. However, it raises the question as to what is and what

happens to the non-product material which accounts for the remaining approximately 5% of the yield.

In the α-naphthylamine dyes currently being produced, the α-naphthylamine is almost always coupled to an aromatic amine which has been previously diazotized. The general coupling reaction with α-naphthylamine (or α-naphthylamine hydrochloride) can be depicted as indicated in the following equation:

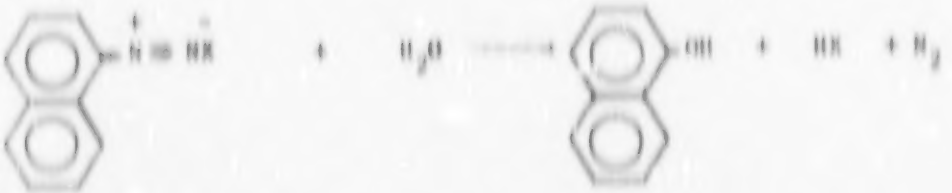


chloride may exist in the reactor in uncoupled form. With the exception of the dye, Disperse Black 1, the batch is diazotized again for additional coupling of intermediates. This type of diazotization is a very complete reaction, so virtually all of the coupled and uncoupled α-naphthylamine will be diazotized as follows:



As described in Section V-B, ice is added to the reactor to maintain a temperature range of 0°-5°C to prevent decomposition of the diazonium chlorides. After the coupling reaction of the final intermediate, a small percentage of unreacted diazonium chlorides will still exist, and when they emerge from the reactor in the "mother liquid," they will warm up and decompose.

Diazonium salts in acid solution decompose smoothly by a unimolecular reaction with liberation of nitrogen and formation of phenol derivatives. Small amounts of haloaromatics may also be obtained in the decomposition of diazonium halides. For α-naphthylamine, the reactions are illustrated below (Donaldson, 1958):

(1) 

(2)

Therefore, there will be virtually no free α-naphthylamine in the "mother liquid" after it has emerged from the reactor. The actual quantity of free α-naphthylamine has been suggested to be in the "parts per billion" range (Boyd, 1975-1976; Morgan, 1975; Jackobets, 1975).

The water effluent from the dye processes will contain salt (used for salting-out the dye), some unprecipitated dye, some acid, and very small amounts of α-naphthylamine and decomposed diazonium chlorides. The effluent from the dye plants is either released to the city or country sewage system or to the ocean (see Table V-9). Although very little information is available on the biodegradability of α-naphthylamine in water treatment plants, Lutin and coworkers (1975) have suggested that the chemical is either resistant or an inhibitor to the action of activated sludge.

In summary, the amount of α-naphthylamine released to the environment from dye manufacturing plants is probably very small. However, if the chemical is being released, it probably will not be removed by water treatment.

VII. Environmental Assessment

α-Naphthylamine is a suspected carcinogen and, therefore, considerable caution should be exercised so that workers are not exposed to the chemical or that the chemical is not released to the environment where human contact may also be possible. Standards established by the Occupational Safety and Health Administration (see Appendix A) have controlled the occupational exposure to α-naphthylamine and have also had an impact on reducing contamination of the external environment. For example, the standards state that: "Any equipment, material, or other item taken into or removed from a regulated area [any area where α-naphthylamine is manufactured, processed, used, repackaged, released, handled, or stored] shall be done so in a manner that does not cause contamination in nonregulated areas or the external environment" (Anon., 1978 c).

As indicated in the previous section, the OSHA regulations, along with current industry practices, appear to have eliminated the release of α-naphthylamine to the external environment. All wastes from the manufacturing process (3-4 million pounds a year) are incinerated. α-Naphthylamine produced in the United States is only available in the molten form and can only be handled in closed systems. Small amounts (0.25-0.50 million pounds a year) of solid flaked α-naphthylamine are imported for use in the dye industry, but handling of that material must also meet OSHA standards. As described in detail in the previous section, the use of α-naphthylamine as a chemical intermediate for the herbicide naptalam (80-90% of the total production) and for the synthesis of various dyes (10-20% of the total production) does not appear to result in any release of α-naphthylamine to the environment.

However, firm conclusions on the potential release of α-naphthylamine from these intermediate uses require effluent monitoring data that is not available at this time.

All the previous discussions have concentrated on potential sources of release of α-naphthylamine, since it is the suspected carcinogen. However, it is possible that an α-naphthylamine-derived compound could be released to the environment and then degrade to α-naphthylamine. At least two possible sources of this type of contamination seem possible.

Takemura et al. (1965) have detected α-naphthylamine in the Sumida River. They concluded that the contamination was due to wastes from dye and pigment factories along the river. However, they suggested that the α-naphthylamine was not necessarily discharged in the waste, but may have been produced by reduction of the azo-dyes in the wastes by H_2S or SO_2 in the river. The authors demonstrated that aromatic amines could be formed by bubbling H_2S through a pure azo-dye solution. Since the water effluents from α-naphthylamine-derived dyes contain some unprecipitated dye and it is unknown if the treatment process used will remove the dyes, the possibility is quite high that the dyes may reach rivers or the ocean. However, the water system receiving the dyes would have to be very polluted so that H_2S or SO_2 (or a reducing environment) would be available for conversion of the dye to α-naphthylamine.

The other possible indirect source of α-naphthylamine deserves considerable evaluation. Naptalam (N-1-Naphthylphthalamic acid) is produced and consumed in approximately six million pounds annually. It is used as a pre-emergent herbicide with soybeans and peanuts and thus is widely released into the environment. The environmental fate of naptalam has not been studied and reported

in the open literature, although some information must have been developed for EPA registration purposes. Naptalam does hydrolyze to naphthylamine at pH 9.5 or above (Smith and Stone, 1953; Spencer, 1968). If all the naptalam hydrolyzed to α-naphthylamine, the annual use of naptalam would be the source of three million pounds of α-naphthylamine in the environment.

Appendix A

Occupational Safety and Health Standards and Interpretations

1910.1004——ALPHA-NAPHTHYLAMINE

§ 1910.994 alpha-Naphthylamine.

(a) *Scope and application.* (1) This section applies to any area in which alpha-Naphthylamine (Chemical Abstracts Service Registry Number 134327) is manufactured, processed, repackaged, released, handled, or stored, but shall not apply to transshipment in sealed containers, except for the labeling requirements under paragraphs (d)(1)(i), (3), and (4) of this section.

(2) This section shall not apply to solid or liquid mixtures containing less than 1% percent by weight or volume of alpha-Naphthylamine.

(3) This section shall not apply to operations involving the destructive distillation of carbonaceous materials, such as occurs in coke ovens.

(b) *Definitions.* For the purposes of this section: (1) "Absolute filter" is one capable of retaining 99.97 percent of a monodisperse aerosol of 0.3 μm particles.

(2) "Authorized employee" means an employee whose duties require him to be in the regulated area and who has been specifically assigned by the employer.

(3) "Clean change room" means a room where employees put on clean clothing and/or protective equipment in an environment free of alpha-Naphthylamine. The clean change room shall be contiguous to and have an entry from a shower room, when the shower room facilities are otherwise required in this section.

(4) "Closed system" means an operation involving alpha-Naphthylamine where containment prevents the release of alpha-Naphthylamine into regulated areas, nonregulated areas, or the external environment.

(5) "Decontamination" means the inactivation of alpha-Naphthylamine or its safe disposal.

(6) "Director" means the Director, National Institute for Occupational Safety and Health, or any person directed by him or the Secretary of Health, Education, and Welfare to act for the Director.

(7) "Disposal" means the safe removal of alpha-Naphthylamine from the work environment.

(8) "Emergency" means an unforeseen circumstance or set of circumstances resulting in the release of alpha-Naphthylamine which may result in exposure to or contact with alpha-Naphthylamine.

(9) "External environment" means any environment external to regulated and nonregulated areas.

(10) "Isolated system" means a full, enclosed structure other than the vessel of containment of alpha-Naphthylamine, which is impervious to the passage of alpha-Naphthylamine and which would prevent the entry of alpha-Naphthylamine into regulated areas, nonregulated areas, or the external environment, should leakage or spillage from the vessel of containment occur.

(11) "Laboratory type hood" is a device enclosed on three sides and the top and bottom, designed and maintained to draw air inward at an average inward face velocity of 150 feet per minute with a minimum of 100 feet per minute, designed, constructed and maintained in such a way that an operation involving alpha-Naphthylamine within the hood does not require the insertion of any portion of any employees' body other than the hands and arms.

(12) "Nonregulated area" means any area under the control of the employer where entry and exit is neither restricted nor controlled.

(13) "Open-vessel system" means an operation involving alpha-Naphthylamine in an open vessel, which is not in an isolated system, a laboratory type hood, nor in any other system affording equivalent protection against the entry of alpha-Naphthylamine into regulated areas, nonregulated areas, or the external environment.

(14) "Protective clothing" means clothing designed to protect an employee against contact with or exposure to alpha-Naphthylamine.

(15) "Regulated area" means an area where entry and exit is restricted and controlled.

(c) *Requirements for areas containing alpha-Naphthylamine.* A regulated area shall be established by an employer where alpha-Naphthylamine is manufactured, processed, used, repackaged, released, handled or stored. All such areas shall be controlled in accordance with the requirements for the following category or categories describing the operation involved. (1) *Isolated systems.* Employees working with alpha-Naphthylamine within an isolated system, such as a "glove box," shall wash their hands and arms upon completion of the assigned task and before engaging in other activities not associated with the isolated system.

(2) *Closed system operation.* Within regulated areas where alpha-Naphthylamine is stored in sealed containers, or contained in a closed system, including piping systems, with any sample ports or openings closed while alpha-Naphthylamine is contained within: (i) Access shall be restricted to authorized employees only;

(ii) Employees shall be required to wash their hands, forearms, face and neck upon each exit from the regulated area, either at the point of exit and before engaging in other activities;

(3) *Open vessel system operations.* Open vessel system operations as defined in paragraph (b)(13) of this section are prohibited.

(6) Transfer from a closed system, charging or discharging animal operations, or otherwise opening a closed system in operations involving laboratory type hoods or in locations where alpha-Naphthylamine is contained in an otherwise closed system, but is transferred, charged, or discharged into other normally closed containers, the provisions of this subparagraph shall apply.

(i) Access shall be restricted to authorized employees only.

(ii) Each operation shall be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation. Exhaust air shall not be discharged to regulated areas, nonregulated areas or the external environment unless decontaminated. Clean makeup air shall be introduced in sufficient volume to maintain the correct operation of the local exhaust system.

(iii) Employees shall be provided with, and required to wear clean, full body protective clothing, including coveralls or long-sleeved shirt and pants, and shoe covers and gloves prior to entering a regulated area.

(iv) Employees engaged in alpha-Naphthylamine handling operations shall be provided with and required to wear and use a half-face, filter type respirator for dusts, mists, and fumes in accordance with § 1910.134. A respirator affording higher levels of protection may be substituted.

(v) Prior to each exit from a regulated area, employees shall be required to remove and leave protective clothing and equipment at the point of exit and at the last exit of the day, to place used clothing and equipment in impervious containers at the point of exit for purposes of decontamination or disposal. The contents of such impervious containers shall be identified as required under paragraphs (d)(2), (d), and (d) of this section.

(vi) Employees shall be required to wash hands, forearms, face, and neck upon each exit from the regulated area, close to the point of exit, and before engaging in other activities.

(vii) Employees shall be required to shower after the last exit of the day.

(viii) Drinking fountains are prohibited in the regulated area.

(3) Maintenance and decontamination activities. In absence of leaks or spills, maintenance of regularly operating decontaminated systems of equipment, or any operations involving work in an area under direct control with alpha-Naphthylamine, could result in such exposures, employee cleaning that area shall:

(i) Be provided with and required to wear clean, impervious garments, including gloves, boots and continuous air supplied hood in accordance with § 1910.134.

(ii) Be decontaminated before removing the protective garments and hood.

(iii) Be required to shower upon removing the protective garments and hood.

(4) Laboratory activities. The requirements of this subparagraph shall apply to research and quality control activities involving the use of alpha-Naphthylamine. All mechanical pipetting aids shall be used for all pipetting procedures.

(i) Experimental procedures and equipment which could produce aerosols shall be confined to laboratory-type hoods or glove boxes.

(ii) Surfaces on which alpha-Naphthylamine is handled shall be protected from contamination.

(iii) Contaminated wastes and animal carcasses shall be collected in impervious containers which are labeled and decontaminated prior to removal from the work area. Such wastes and carcasses shall be incinerated in such a manner that no carcinogenic products are released.

(iv) All other forms of alpha-Naphthylamine shall be inactivated prior to disposal.

(v) Laboratory vacuum systems shall be protected with high efficiency scrubbers or with disposable absolute filters.

(vi) Employees engaged in animal support activities shall be (a) provided with and required to wear a complete protective clothing change (clean each day, including coveralls or pants and shirt, foot covers, head covers, gloves, and appropriate respirators protective equipment or devices); and

(b) Prior to each exit from a regulated area, employees shall be required to remove and leave protective clothing and equipment at the point of exit and at the last exit of the day, to place used clothing and equipment in impervious containers at the point of exit for purposes of decontamination or disposal. The contents of such impervious containers shall be identified as required under paragraphs (d)(2), (d), and (d) of this section.

(c) Required to wash hands, forearms, face, and neck upon each exit from the regulated area, close to the point of exit, and before engaging in other activities; and

(d) Required to shower after the last exit of the day.

(vii) Employees other than those engaged in animal support activities shall be (a) provided with and required to wear, a clean change of appropriate laboratory clothing, such as an solid front gowns, surgical scrub suit, or fully buttoned laboratory coat.

(5) Prior to each exit from a regulated area, employees shall be required to remove and leave protective clothing and equipment at the point of exit and at the last exit of the day, to place used clothing and equipment in impervious containers at the point of exit for purposes of decontamination or disposal. The contents of such impervious containers shall be disposed of as required under paragraphs (g) (3), (8), and (9) of this section.

(6) Required to wash hands, forearms, face and neck upon each exit from the regulated area close to the point of exit and before engaging in other activities.

(7) Air pressure in laboratory areas and animal rooms where alpha-Naphthylamine is handled and bioassay studies are performed shall be negative in relation to the pressure in surrounding areas. Exhaust air shall not be discharged to regulated areas, nonregulated areas or the external environment unless decontaminated.

(8) There shall be no connection between regulated areas and any other areas through the ventilation system.

(9) A current inventory of alpha-Naphthylamine shall be maintained.

(10) Ventilated apparatus such as laboratory type hoods shall be tested at least semi-annually or immediately after ventilation modification or maintenance operations, by personnel fully qualified to certify correct containment and operation.

(f) *Regulated areas—(1) Employee identification.* A daily roster of employees entering regulated areas shall be established and maintained. The roster or a summary of the rosters shall be retained for a period of 30 years. The rosters and/or summaries shall be provided upon request to authorized representatives of the Assistant Secretary and the Director. In the event that the employee ceases business without a successor, rosters shall be forwarded by registered mail to the Director.

(2) *Emergencies.* In an emergency, immediate measures, including, but not limited to, the requirements of subparagraphs (1), (4), (5), (7), (9), and (10) of this subparagraph shall be implemented. The potentially affected area shall be evacuated as soon as the emergency has been determined.

(3) Hazardous conditions created by the emergency shall be eliminated and the potentially affected area shall be decontaminated prior to the resumption of normal operations.

(4) Special medical surveillance by a physician shall be instituted within 24 hours for employees present in the potentially affected area at the time of the emergency. A report of the medical surveillance and any treatment shall be included in the incident report, in accordance with paragraph (f) (13) of this section.

(5) Where an employee has a known contact with alpha-Naphthylamine such employee shall be required to shower as soon as possible, unless contraindicated by physical injuries.

(6) An incident report on the emergency shall be reporting as provided in paragraph (f) (13) of this section.

(7) *Hygiene facilities and practices.* (i) Storage or consumption of food, storage or use of containers of beverages, storage or application of cosmetics, storage of smoking materials, tobacco products or other products for chewing, or the chewing of such products are prohibited in regulated areas.

(ii) Where employees are required by this section to wash, washing facilities shall be provided in accordance with § 1910.141(d)(2) and (3)(i) through (vi).

(iii) Where employees are required by this section to shower, shower facilities shall be provided in accordance with § 1910.141(d)(3).

(iv) Where employees wear protective clothing and equipment, clean change rooms shall be provided in accordance with § 1910.141(d)(3). For the number of such employees required to change clothes.

(v) Where toilets are in regulated areas, such toilets shall be in a separate room.

(8) *Contamination control.* (i) Regulated areas, except for outdoor systems, shall be maintained under pressure negative with respect to nonregulated areas, or exhaust ventilation may be used to satisfy this requirement. Clean make-up air in equal volume shall replace air removed.

(ii) Any equipment, material, or other items taken into or removed from a regulated area shall be done so in a manner that does not cause contamination in nonregulated areas or the external environment.

(iii) Decontamination procedures shall be established and implemented to remove alpha-Naphthylamine from the surfaces of materials, equipment and the decontamination facility.

(iv) Dry sweeping and dry mopping are prohibited.

(9) *Signs, labels and instructions.* (i) Signs at the entrances to regulated areas shall be posted with signs bearing the legend:

Caution Bioassay Area!
Authorized Personnel Only

(iii) Entrances to regulated areas containing operations covered by paragraph (c)(5) of this section shall be posted with signs bearing the legend:

Cancer-Hazard! Avoid Exposure in This Area. Impervious Suit, Including Gloves, Boots and Air Supplied Hood Required at All Times. Authorized Personnel Only

(iii) Appropriate signs and instructions shall be posted at the entrance to, and exit from, regulated areas, informing employees of the procedures that must be followed in entering and leaving a regulated area.

(2) *Container contents identification.* (i) Containers of alpha-Naphthylamine and containers required under paragraphs (c)(3)(iv) and (c)(8)(vi)(b), and (c)(8)(vii)(b) of this section which are accessible only to, and handled only by, authorized employees, or by other employees trained in accordance with subparagraph (5) of this paragraph, may have contents identification limited to a generic or proprietary name, or other proprietary identification, of the carcinogen and percent.

(ii) Containers of alpha-Naphthylamine and containers required under paragraphs (c)(3)(iv), (c)(8)(vi)(b), and (c)(8)(vii)(b) of this section which are accessible to, or handled by employees other than authorized employees or employees trained in accordance with subparagraph (5) of this paragraph shall have contents identification which includes the full chemical name and Chemical Abstracts Service Registry number as listed in paragraph (a)(1) of this section.

(iii) Containers shall have the warning words "CANCER-HAZARD" AVOID EXPOSURE" displayed immediately under or adjacent to the contents identification.

(iv) Containers which have alpha-Naphthylamine contents with corrosive or irritating properties shall have label statements warning of such hazards, noting, if appropriate, particularly sensitive or affected portions of the body.

(3) *Lettering.* Lettering on signs and instructions required by subparagraph (1) of this paragraph shall be a minimum letter height of 2 inches. Labels on containers required under this section shall not be less than ½ the size of the largest lettering on the package, and not less than 8 point type in any instance: *Provided*, That no such required lettering need be more than 1 inch in height.

(4) *Prohibited statements.* No statement shall appear on or near any required sign, label, or instruction which contradicts or detracts from the effect of any required warning, information or instruction.

(5) *Training and indoctrination.* (i) Each employee prior to being authorized to enter a regulated area, shall receive a training and indoctrination program including, but not necessarily limited to:

(a) The nature of the carcinogenic hazards of alpha-Naphthylamine, including local and systemic toxicity;

(b) The specific nature of the operation involving alpha-Naphthylamine which could result in exposure;

(c) The purpose for and application of the medical surveillance program, including, as appropriate, methods of self-examination;

(d) The purpose for and application of decontamination practices and purposes;

(e) The purpose for and significance of emergency practices and procedures;

(f) The employee's specific role in emergency procedures;

(g) Specific information to aid the employee in recognition and evaluation of conditions and situations which may result in the release of alpha-Naphthylamine;

(h) The purpose for and application of specific first aid procedures and practices.

(ii) A review of this section at the employee's first training and indoctrination program and annually thereafter.

(iii) Specific emergency procedures shall be prescribed and posted, and employees shall be familiarized with their terms and rehearsed in their application.

(iv) All materials relating to the program shall be provided upon request to authorized representatives of the Assistant Secretary and the Director.

(6) *Reports.* (i) *Operations.* Not later than March 1, 1978, the information required in subdivisions (i), (ii), (iii), and (iv) of this subparagraph shall be reported in writing to the nearest OSHA Area Director. Any changes in such information shall be similarly reported in writing within 15 calendar days of such changes. (i) A brief description and identification of the area(s) regulated and the address of each regulated area;

(ii) The name(s) and other identifying information as to the presence of alpha-Naphthylamine in each regulated area;

(iii) The number of employees in each regulated area during normal operations, including maintenance activities; and

(iv) The manner in which alpha-Naphthylamine is present in each regulated area, e.g. whether it is manufactured, processed, used, repackaged, released, stored, or otherwise handled.

(2) Accidents, incidents which result in the release of alpha Naphthylamine into any area where employees may be potentially exposed shall be reported in accordance with this subparagraph: (i) A report of the occurrence of the incident and the facts obtainable at that time including a report on any medical treatment of affected employees shall be made within 24 hours to the nearest OSHA Area Director.

(ii) A written report shall be filed with the nearest OSHA Area Director within 15 calendar days thereafter and shall include:

(a) A specification of the amount of material released, the amount of time involved, and an explanation of the procedure used in determining this figure;

(b) A description of the area involved, and the extent of known and possible employee exposure and area contamination; and

(c) A report of any medical treatment of affected employees, and any medical surveillance program implemented; and

(d) An analysis of the circumstances of the incident, and measures taken or to be taken, with specific completion dates to avoid further similar releases.

(e) *Medical surveillance.* At no cost to the employee, a program of medical surveillance shall be established and implemented for employees considered for assignment to enter regulated areas, and for authorized employees. (1) *Examinations.* (i) Before an employee is assigned to enter a regulated area, a preassignment physical examination by a physician shall be provided. The examination shall include the personal history of the employee, family and occupational background, including genetic and environmental factors.

(ii) Authorized employees shall be provided periodic physical examinations, not less often than annually, following the preassignment examination.

(iii) In all physical examinations, the examining physician shall consider whether there exist conditions of increased risk, including reduced immunological competence, those undergoing treatment with steroids or cytotoxic agents, pregnancy and cigarette smoking.

(2) *Records.* (i) Employers of employees examined pursuant to this paragraph shall cause to be maintained complete and accurate records of all such medical examinations. Records shall be maintained for the duration of the employee's employment. Upon termination of the employee's employment, including retirement or death, or in the event that the employer ceases business without a successor, records, or notarized true copies thereof, shall be forwarded by registered mail to the Director.

(ii) Records required by this paragraph shall be provided upon request to authorized representatives of the Assistant Secretary or the Director, and upon request of an employee or former employee, to a physician designated by the employee or to a new employer.

(iii) Any physician who conducts a medical examination required by this paragraph shall furnish to the employer a statement of the employee's suitability for employment in the specific exposure

Appendix B

Material Safety Data Sheet for Alpha-Naphthylamine

U.S. DEPARTMENT OF LABOR

OCCUPATIONAL SAFETY & HEALTH ADMINISTRATION

MATERIAL SAFETY DATA SHEET

SECTION I

MANUFACTURER'S NAME	EMERGENCY TELEPHONE NO.
E. I. du Pont de Nemours & Co.	(302) 774-7500
Chemicals Division, Wilmington, Delaware 19898	
TRADE NAME AND SYNONYMS	
Fast Red AL Salt	Naphthol AS-BI Phosphoric Acid
CHEMICAL FAMILY	FORMULA
Aromatic Amine	$C_{17}H_{14}NO_5P$

SECTION II HAZARDOUS INGREDIENTS

PAINTS, PRESERVATIVES, & SOLVENTS	%	TLV (Units)	ALLOYS AND METALLIC COATINGS	%	TLV (Units)
PIGMENTS			BASE METAL		
CATALYST			ALLOYS		
VEHICLE			METALLIC COATINGS		
SOLVENTS			FILLER METAL PLUS COATING OR CORE FLUX		
ADDITIVES			OTHERS		
OTHERS					
HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES				%	TLV (Units)
This section not applicable					
alpha-Naphthylamine may contain up to 0.5% beta-Naphthylamine (5,000 ppm)					

SECTION III PHYSICAL DATA

BOILING POINT (°F.)	572° F.	SPECIFIC GRAVITY (H_2O = 1)	1.2
VAPOR PRESSURE (mm Hg.)	1mm/210°	PERCENT VOLATILE BY VOLUME (%) Not applicable	
VAPOR DENSITY (AIR = 1)	4.93	EVAPORATION RATE (Butyl Acetate = 1) Not applicable	
SOLUBILITY IN WATER	slightly		
APPEARANCE AND ODOR Tan to brown flakes tends to darken on storage. Characteristic amine odor.			

SECTION IV FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method used) 312° F. (C.C.)	FLAMMABLE LIMITS Not available	LEL	UEL
EXTINGUISHING MEDIA Water, CO2, foam			
SPECIAL FIRE FIGHTING PROCEDURES If product is exposed to fire or intense heat toxic fumes may be generated. If exposure is likely complete body protection may be required.			
UNUSUAL FIRE AND EXPLOSION HAZARDS None except fumes noted above.			

NOTICE FROM DU PONT

The data in this Material Safety Data Sheet relates only to the specific material designated herein and does not relate to use in combination with any other material or in any process.

SECTION V HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE: Not available

EFFECTS OF OVEREXPOSURE: Because alpha-Naphthylamine may contain the carcinogen beta-Naphthylamine exposure to the commercial product must be minimized. Prolonged chronic exposure may result in bladder tumors. (See below*)

EMERGENCY AND FIRST AID PROCEDURES: Wash exposed parts of body with soap and water. Obtain medical attention for cyanosis. Periodic medical examination of workers with potential exposure to alpha-Naphthylamine should be performed.

SECTION VI REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID
	STABLE	X	

INCOMPATABILITY (Materials to avoid): Oxidizing agents

HAZARDOUS DECOMPOSITION PRODUCTS: Oxides of nitrogen

HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR	X	

SECTION VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED: Use dust respirator if dust is present. Clean up area followed by washing to remove residual material.

WASTE DISPOSAL METHOD: Product may be incinerated.

SECTION VIII SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify type): (See below)

VENTILATION	LOCAL EXHAUST	X	SPECIAL
	MECHANICAL (General)		OTHER

PROTECTIVE GLOVES	Butyl rubber	EYE PROTECTION	Side shield safety glasses

OTHER PROTECTIVE EQUIPMENT: Where exposure is likely, complete body protection such as "Chem-Proof Suits" is required.

SECTION IX SPECIAL PRECAUTIONS

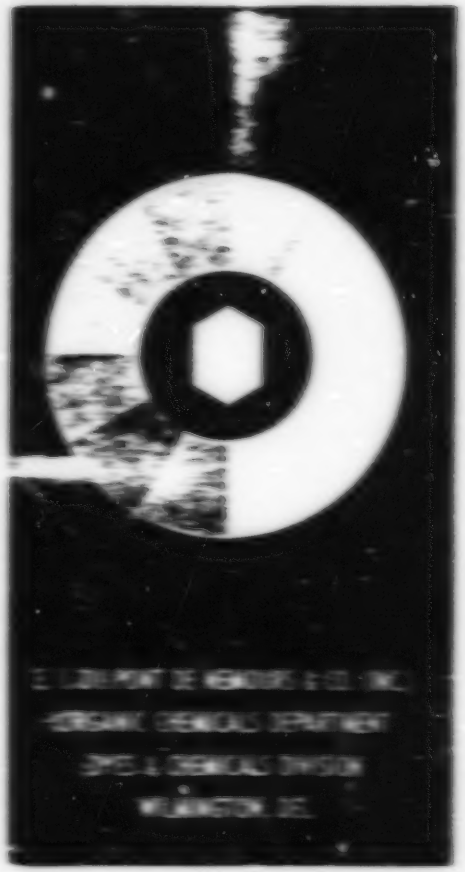
PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING: Store material in well ventilated area. Direct body exposure to fumes and dust must be prevented.

OTHER PRECAUTIONS:

* Exposure to alpha-Naphthylamine may also cause cyanosis.

Labelling for α-Naphthylamine shipment

62



LOT_____ DU PONT PKG_____

alpha-NAPHTHYLAMINE TECH. 134327

(Contains up to 0.5% beta-Naphthylamine)

CANCER SUSPECT AGENT

WARNING! Harmful Dust and Vapor
Repeated Inhalation or Skin Absorption
May Result in Bladder Tumors

Avoid breathing dust or vapor.
Use only with adequate ventilation.
Avoid contact with skin.
Wash thoroughly after handling.
Wear fresh clothing daily. Take a hot shower after work, using plenty of soap.
Keep container closed.
Store in a cool dry place.

SPILL: Sweep up; remove to chemical waste area.
Before using, read NIOA Chemical Safety Data Sheet SD-32, beta-Naphthylamine.

MADE IN U.S.A.

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